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# ALLEN'S COMMERCIAL ORGANIC ANALYSIS

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## FOURTH EDITION REWRITTEN AND REVISED

EDITED BY HENRY LEFFMANN, M. A., M. D., PROFESSOR OF CHEMISTRY AND TOXICOLOGY IN THE WOMAN'S MEDICAL COLLEGE OF PENNSYLVANIA; W. A. DAVIS, B. Sc., A. C. G. I., FORMERLY LECTURER AND ASSISTANT IN THE CHEMICAL RESEARCH LABORATORY, CITY AND GUILDS COLLEGE, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON; AND SAMUEL S. SADTLER, S. B., VICE-PRESIDENT OF THE AMERICAN ELECTRO-CHEMICAL SOCIETY; MEMBER AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

In many respects this edition of Allen is a new work. The field of Commercial Organic Analysis has been so enlarged and specialised during the last few years that it has been found necessary to rewrite many parts and add much new matter. Obsolete methods are omitted; what little of the old text remains has been carefully revised and many new illustrations added.

To accomplish the object in view, namely, the furnishing of a modern work of the greatest practical value to the analyst, it was deemed advisable to secure the services of an English and an American editor and to organise a corps of writers particularly versed in the subjects discussed.

The general arrangement of the volumes remains as before, only such changes have been made as will bring the text into line with the latest scientific classification. Great care has been exercised by the editors and contributors in the choice of methods and only those of the highest degree of accuracy and rapidity selected. Effort has been made to secure uniformity in weights and measures, nomenclature and abbreviations. References are to original sources, not to translations or abstracts.

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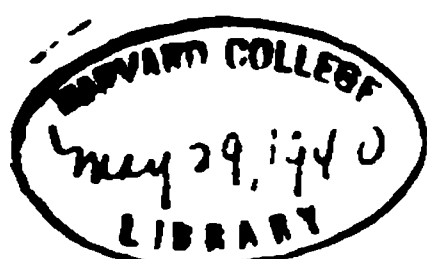
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## PREFACE

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Since the revision of this work was first undertaken in 1907, a considerable amount of literature has appeared and many new methods of analysis have been devised. It, therefore, became desirable to issue a supplementary volume bringing the text, especially that of the earlier volumes, up to date. The new articles have, as far as possible, been written by the contributors to the earlier volumes, but, in a few cases, pressure of other work caused by the outbreak of war has made it necessary to entrust the revision to other hands.

A complete general index has also been prepared which is hoped will make the subject matter of the whole work more easily accessible.

The editors and publishers again wish to thank the various contributors for their valuable and willing coöperation in bringing the work to completion.



# CONTENTS.

---

## ALCOHOLS

G. C. JONES.

Methyl Alcohol, 1; Ethyl Alcohol, 4.

## MALT AND BREWING MATERIALS.

G. C. JONES.

Malt, 5; Roasted Malt and Barley, 6; Brown and Crystal Malts, 6; Caramel, 7; Invert Sugar, 7; Starch Sugars, 10; Beer, 11.

## WINES AND SPIRITS.

G. C. JONES.

Physico-chemical Analysis of Wines, 13.

## YEAST.

EMIL SCHLICHTING AND H. WINTHER.

Physical Properties, 15; Classification, 15; Chemical Composition, 15; Fermenting Enzyme, 16; Testing of Yeast, 16; Dry Yeast, 16.

## NEUTRAL ALCOHOLIC DERIVATIVES, 18.

## SUGARS.

W. A. DAVIS.

Solution Densities, 19; Dextrose, 20; Lævulose, 20; Maltose, 20; Refractometer Values, 21; Refractive Index and Water Content of Sugar Solutions, 21; General Methods, 22; Gravimetric Methods for Reducing Sugars, 24; Brown, Morris and Millar's Method, 24; Reducing Power of Dextrose, Lævulose and Invert Sugar, 27; Reducing Power of Maltose, 27; Provisional United States A. O. A. C. Gravimetric Method for Reducing Sugars, 28; Table for Calculating Dextrose, Invert Sugar Alone, Invert Sugar in the Presence of Saccharose, Lactose, and Maltose, 29; Volumetric Methods,

38; Reducing Power of Different Sugars according to Ling and Jones, 39; Estimation of Invert Sugar in the Presence of Cane Sugar, 39; Low's Volumetric Method, Modified, 41; Saccharose, 43; Cane Molasses, 46; Beet Molasses, 47; Estimation of Maltose, 53; Lactose, 57; Table for Calculating Lactose, 58; Pentoses and Pentosans, 62.

### STARCH AND ITS ISOMERIDES.

W. A. DAVIS.

Taka-diastase as an Agent in Estimating Starch, 71; Estimation of Starch by Means of Taka-diastase, 74; Ewer's Method of Estimating Starch in Cereals, 76; Cellulose, 77.

### PAPER AND PAPER-MAKING MATERIALS.

RALPH H. MCKEE.

Wood-pulp, 81; Sulphite Pulp, 84.

### ALIPHATIC ACIDS.

ARTHUR W. THOMAS AND W. A. DAVIS.

Acetic Acid and Vinegar, 90; Pyroligneous Acid, 96; Formic Acid, 97; Oxalic Acid, 97; Succinic Acid, 97; Malic Acid, 98; Tartaric Acid, 99; Citric Acid, 109.

### FIXED OILS, FATS AND WAXES.

C. AINSWORTH MITCHELL.

Extraction of Fat, 117; Unsaponifiable Matter, 118; Bromine and Iodine Absorptions, 118; Oxidation of Oils, 121; Colour Tests of Oils, 122; Catalytic Hydrogenation of Oils—Hardened Oils, 122.

### SPECIAL CHARACTERS AND MODES OF EXAMINING FATS, OILS AND WAXES.

E. R. BOLTON AND CECIL REVIS.

Arachis Oil, 126; Almond and Apricot-kernel Oils, 129; Olive Oil, 131; Tea Seed Oil, 134; Mustard Oil, 134; Cottonseed Oil, 135; Kapok Oil, 135; Sesame Oil, 136; Soja-bean Oil, 137; Candle Nut Oil, 138; Hemp Seed Oil, 139; Pine Nut Oil, 139; Poppy Seed Oil, 139; Safflower Oil, 139; Sunflower Oil, 140; Tung Oils, 140; Japanese Wood Oil, 144; Walnut Oil, 145; Ali-

zarin Oil, Turkey-red Oil, 145; Croton Oil, 146; Bassia Tallow, 146; Shea Nut Oil, 148; Borneo Tallow, 149.

## BUTTER FAT.

CECIL REVIS AND E. R. BOLTON.

Composition of Butter Fat, 152; Qualitative Tests, 154; Estimation of Salt, 162; Estimating the Percentage of Curd, 162; Oleomargarine, 166; Hardened Fats, 173; Ghee, 175.

## LARD.

C. AINSWORTH MITCHELL.

Detection of Beef and Mutton Fats in Lard, 178.

## LINSEED OIL.

C. A. KLEIN.

Cultivation, 180; Preparation of Oil from Seed, 180; Examination of Seeds, 181; Linseed Cake, 182; Technical Applications, 184; Chemical Composition, 184; Preparation of Sample for Analysis, 186; Foots, 186; Break Test, 186; Specific Gravity, 187; Ash, 187; Free Fatty Acids, 187; Unsaponifiable Matter, 188; Iodine Value, 188; Bromine Values, 189; Insoluble Hexabromides, 189; Qualitative Test, 189; Quantitative Methods, 190; Refractive Index, 192; Oxygen Absorption and Drying Test, 192; Drying on Glass, 195; Qualitative Detection of Adulterants in Linseed Oil, 195; Interpretation of Abnormal Characteristics, 196; Effect of Storage, 196; Hydrolysis of Glycerides, 196; Oil Extracted from Paints, 197; Drying of Linseed Oil, 198; Boiled Oil, 200; Blown Oils, 201.

## SOAPS.

J. R. POWELL.

Water, 204; Separation of Substances Soluble in Petroleum Ether, 205; Estimation of Fatty Acids, 205; Examination of Fatty Acids, 206; Estimation of Free Alkali, 206; Matter Insoluble in Alcohol, 207; Fillers Insoluble in Water, 208; Estimation of Special Constituents, 208; Cresols, 208; Soap Powders, Scouring Powders, and Scouring Soaps, 209.

## GLYCEROL.

W. A. DAVIS.

Specific Gravity, 211; Analysis of Crude Glycerol, 211; Sampling, 211;



Analysis, 212; Acetin Process for Glycerol Estimation, 214; Dichromate Process for Glycerol Estimation, 217; Instructions for Calculating Actual Glycerol Content, 218; British Standard Specifications for Crude Glycerins, 219; Soap Lyes, Crude Glycerin, 219; Saponification Crude Glycerin, 219; Pure Glycerin, 220; Aldehydic Impurities in Glycerol, 221; Estimation of Glycerol in Wines, 221; Estimation of Glycerol in Fats, 222.

### **CHOLESTEROL.**

**J. ADDYMAN GARDNER.**

Estimation of Cholesterol in Animal Tissues, 223; Estimation of Cholesterol and Cholesterol Esters in an Extract, 224.

### **WOOL, GREASE AND CLOTH OILS, 228.**

**AUGUSTUS H. GILL.**

### **HYDROCARBONS.**

**R. LESSING.**

Physical Methods of Separation, 229; Chemical Methods, 232; Olefines, 233; Aromatic Hydrocarbons, 234; Naphthenes, 236; Paraffins, 238.

### **BITUMENS.**

**S. S. SADTLER.**

Asphalt, 240; Method of Extracting Bitumens from Binding Courses, Topekas, etc., 241; Ductility, 242; Melting-point, 242; Apparatus, 242; Manipulation, 242; Float Test, 243; Drip Point, 243; Fluxes, 243; Roofing Papers, 244; Estimation of Paraffin in Asphaltum, 244; Mineral Oils, 247; Proposed Provisional Tests for Lubricants, 251; Cyclic Hydrocarbons, 259; Method of Testing Drip Oils, 261; Distillation Test, 262.

### **NAPHTHALENE AND ITS DERIVATIVES.**

**W. A. DAVIS.**

Naphthalene in Coal Gas, 266; Estimation of Naphthalene in Spent Oxide, 268; Estimation of  $\beta$ -Naphthol, 269; Pharmacopœia Requirements, 269.

### **PHENOLS.**

**S. S. SADTLER.**

Estimation of Phenol in Crude Carbohc Acid and Tra Oils, 270; Effect of Temperature, Acid Concentration and Time on Bromination of Phenol in

Quantitative Estimations, 271; The Value of the Higher Phenols in Wood-preserving Oils, 271; Behaviour of Phenols, Naphthols and Phenolcarboxylic Acids towards Tetravalent Titanium, 272; Cresols, 272; Estimation of *m*-Cresol in Cresol Mixtures, Raschig's Method, 273; Creosote, 275; Tar Acids, 275; Coke Test, 276; Antiseptic Properties of Creosote, 276; Antiseptic Tests of Wood-preserving Oils, 276; Detection of Natural Asphaltum and Petroleum Pitch in Residues from the Distillation of Coal Tar, 277; Application of the Dimethyl Sulphate Test for Detecting Small Amounts of Petroleum or Asphalt Products in Tars, 278.

## AROMATIC ACIDS.

EDWARD HORTON.

Phenol-*p*-sulphonic Acid, 279; Benzoic Acid and its Derivatives, 279; Metallic Benzoates, 285; Benzoic Aldehyde, 286; Benzaldehyde, 286; Saccharin, 288; Cinnamic Acid and its Derivatives, 291;  $\beta$ -Phenyl-acrylic Acid, 291; Cinnamic Aldehyde, 292; Coumarin, 293; Aromatic Balsams, 294; Cinnamic Balsams, 295; Peruvian Balsam, 295; Tolu Balsam, 297; Liquid Storax, 297; Salicylic Acid and its Allies, 299; Commercial Salicylic Acid, 299; Metallic and Alkaloidal Salicylates, 304; Salicylic Esters, 305; Derivatives of Salicylic Acid, 306; Dihydroxybenzoic Acid and Their Allies, 306; Vanillin, 306.

## RESINS.

ERNEST J. PARRY.

Copal, 310; Dammar Resin, 310; Dragon's Blood, 311; Guaiacum, 311; Shellac, 311; Canada Balsam, 312; Copaiba, 313; Ammoniacum, 315; Asafoetida, 316; Elemi, 318; Galbanum, 318; Myrrh, 318.

## INDIA-RUBBER, RUBBER SUBSTITUTES AND GUTTA-PERCHA.

E. W. LEWIS.

India-rubber, 320; Resins, 320; Estimation of India-rubber, 321; Insoluble Impurities, 322; Nitrogen, 322; Pyridine Extraction, 322; Mineral Matter, 323; Estimation of Total Sulphur, 323.

## ESSENTIAL OILS.

ERNEST J. PARRY.

Hydrocarbons of Essential Oils, 324; Terpenes Proper, 324; Sesquiterpenes, 325; Estimation of Free Acids in Essential Oils, 325; Estimation of Alcohols

in Essential Oils, 328; Esters in Essential Oils, 330; Estimation of Aldehydes and Ketones, 336; Estimation of Citral, 337; Refractive Indices of Essential Oils, 339; Alcohols of Geraniol Series, 341; Cyclic Terpene Alcohols, 342; Aldehydes of the Geraniol Series, 344.

### SPECIAL CHARACTERISTICS OF ESSENTIAL OILS.

ERNEST J. PARRY.

Andropogon Oils, 345; Citronella Oil, 345; Lemon-grass Oil, 346; Palmarosa Oil and Ginger-grass Oil, 347; Vetivert Oil, 347; Almond Oil, 349; Angelica Oil, 349; Aniseed Oil, 351; Bay Oil, 352; Bergamot Oil, 352; Buchu Oil, 353; Calamus Oil, 353; Camphor Oil, 353; Cardamon Oil, 354; Cassia and Cinnamon Oils, 354; Champaca Oil, 357; Clove Oil, 358; Oil of Cubebs, 358; Cypress Leaf Oil, 359; Eucalyptus Oil, 359; Fennel Oil, 360; Geranium Oil, 361; Ginger Oil, 362; Hop Oil, 362; Juniper Berry Oil, 363; Lavender Oils, 363; Lemon Oil, 365; Lime Oil, 365; Linalol Oil, 366; Orange Oil, 368; Oil of Rue, 369; Petitgrain Oil, 369; Peppermint Oil, 370; Spearmint Oil, 372; Pine Needle Oil, 372; Rose Oil, 373; Rosemary Oil, 374; Santalwood Oil, 375; Thyme Oil, 376; Turpentine Oil, 377; Wintergreen Oil, 381; American Wormseed Oil, 382; Ylang-ylang Oil, 382; Cananga Oils, 382.

### TANNINS.

W. P. DREAPER.

Tannin Materials, 384; Official Method of the American Leather Chemists' Association for the Analysis of Vegetable Materials Containing Tannin, 386; Raw and Spent Materials, 386; Analysis of Extracts, 387; Analysis of Liquors, 389; Temperature, Evaporation and Drying, Dishes, 389; Determination of Total Acidity of Liquors, 390; Official Methods for Sampling Tanning Materials, 390; Tannin Substitutes, 406.

### ANALYSIS OF LEATHER.

W. P. DREAPER.

Official Method for Leather Analysis, 411; Solutions, 411; Determination, 412; Reagents, 412; Provisional Method of Colour Valuation of Tanning Materials, 413; Analysis of American Leathers, 415.

### ANALYSIS OF COLOURING MATERIALS.

W. P. DREAPER.

Chemical Examination of Dyed Fibres, 419; Physical Examination of Dyed Fibres, 419; Fastness of Colours, 419.

## COLOURING MATTERS OF NATURAL ORIGIN.

W. M. GARDNER.

Indigo, 427; Experiments with Rawson's Hydrosulphite Method, 427; Brylinski's Method, 428; Möhlau and Zimmerman's Method, 428; New Methods of Analysis, 429; Improvements in Extraction Apparatus, 430; Experiments upon Acetic Acid Extraction, 432; Estimation of Indigo by Extraction with Pyridine, 433; Analysis of Commercial Indigo-dyed Materials by the Pyrroline and Acetic Acid Methods, 436; Determination of Percentage Colour Effect Due to Indigo, 439; Analysis of Indigo Containing Starch, 446.

## COLOURING MATTERS IN FOODS.

ALBERT F. SEEKER.

Separation of Colours by Means of Immiscible Solvents, 449; Separation of the Seven Colours Permitted in the United States, 453; Read's Test for Detecting Colour in Tea, 454.

## PRINTING INKS.

JOHN B. TUTTLE.

Historical, 456; Composition, 456; Manufacture of Ink, 457; Analysis, 457; Separation of Oil from Pigment, 457; Analysis of the Oil, 458; Oil Constants, 458; Hard Gums, 459; Unsaponifiable Matter, 459; Rosin, 459; Analysis of the Pigment, 460; Blue Inks, 463; Red Inks, 463; Green Inks, 464; Inks of Other Colours, 466; Permanence to Light, 466; Dyes and Lakes, 467; Special Tests, 467.

INKS, 468.

PERCY H. WALKER.

## AMINES AND AMMONIUM BASES.

W. A. DAVIS.

Estimation of Ammonia and Trimethylamine, 469; Hydrazine, 469; Estimation of Antipyrine, 470; Qualitative Tests for Antipyrine and Pyramidine, 470.

## ANILINE AND ITS ALLIES.

S. S. SADTLER.

Estimation of Acetanilide and Phenacetin in Mixture, 472.

**THE NAPHTHYLAMINES AND THEIR ALLIES.****EDWARD HORTON.**

Pyridine, 475; Pyrrole, 476.

**THE VEGETABLE ALKALOIDS.****THOMAS A. HENRY.**

Formation and Function of Alkaloids in Plants, 477; Properties of the Alkaloids, 478; General Principles for Alkaloids, 479.

**VOLATILE ALKALOIDS.****FRANK O. TAYLOR.**

Areca Alkaloids, 480; Arecolidine, 480; Conium Alkaloids, 481; Lobeline, 481; Lupine Alkaloids, 481; Dextro-lupanine, 482; Pomegranate Alkaloids, 483; Sparteine and Other Spartium Alkaloids, 483.

**ESTIMATION OF NICOTINE, 485.****R. W. TONKIN.****ACONITE ALKALOIDS.****FRANCIS H. CARR.**

The Alkaloids of Aconitum Napellus, 487; The Alkaloids of Aconitum Vulparia, 488; Lycaconitine, 488; Myoconine, 488; Lycoctonine, 488; Anthranoyl-lycoctonine, 488; Assay of Aconite and its Preparations, 488; Toxicological Detection of Aconite, 489.

**ATROPINE AND ITS ALLIES.****FRANCIS H. CARR.**

Tropeines and Scopolectines, 490; Hyoscine, 490; Noratropine, 491; Norhyoscyamine, 491; Detection and Estimation of Tropeines, 491.

**COCAINE.****SAMUEL P. SADTLER.**

Separation and Identification of Cocaine, 494; Differentiation of Cocaine from its Substitutes, 495.

## OPIUM ALKALOIDS.

FRANK O. TAYLOR.

Constitution of Opium Bases, 496; Behaviour of Opium Bases with Solvents, 496; Colour Reactions of Opium Bases, 497; Salts of Morphine, 497; Detection and Estimation of Morphine, 497; Apomorphine, 499; Heroin, 499; Dionin, 500; Codeine, 500; Aporeine, 501; Narcotine, 501; Thebaine, 502; Iso-thebaine, 502; Pantopon, 502; Opiopon, 502; Opon, 502; Morphine-narcotine Meconate, 503; Opium, 504; Alkaloids, 504; Adulteration of Opium, 504; Estimation of Morphine in Opium, 504; Normal Opium, 506; Estimation of Morphine in Compounds, 506; Toxicology of Opium and Morphine, 508.

## STRYCHNOS ALKALOIDS.

CHARLES A. VANDERKLEED.

Oil of Nux Vomica, 510; Tests for Brucine in Strychnine, 510; The Assay of Nux Vomica and its Preparations, 512.

## CINCHONA ALKALOIDS.

OLIVER CHICK.

Cinchona Ledgeriana Seeds, 514; Cuprea Bark, 514; Titration of Cinchona Alkaloids, 514; Constitution, 515; General Properties of Cinchona Alkaloids, 515; Quinine, 516; Detection and Estimation of Quinine, 516; Salts of Quinine, 517; Quinine Sulphate, 517; Quinine Hydrochloride, 517; Quinine Dihydrochloride, 517; Quinine Formate, 518; Quinine Glycero-phosphate, 518; Citrate of Iron, Quinine, and Strychnine, Easton's Syrup, 518; Aristoquinine and Euquinine, 519; Hydroquinine, 519; Cinchonine, 520.

## BERBERINE AND ITS ASSOCIATES.

EDWARD HORTON.

Berberine, 521; Hydrastine, 522; Hydrastinine, 524.

## CAFFEINE, TEA AND COFFEE.

J. J. FOX AND P. J. SAGEMAN.

Caffeine, 525; Tea, 528; Coffee, 530.

## OTHER VEGETABLE ALKALOIDS.

GEORGE BARGER AND A. J. EWINS.

Alkaloids of Colchicum, 534; Alkaloid of Laburnum and Furze, 534; Alkaloids of Calabar, 536; Alkaloids of Ergot, 537; Alkaloids of Jaborandi, 537; Solanine Alkaloids, 540; Alkaloid of the Common Broom, 541; Alkaloids of Ipecacuanha, 541.

## GLUCOSIDES.

E. FRANKLAND ARMSTRONG.

Synthetic Glucosides, 545; Cyanogenetic Glucosides, 545; Phytosterolins, 545; Digitalis, 546; Digitoxin and Gitalin, 547; Strophanthin, 547; Sarsaparilla, 548.

## NON-GLUCOSIDAL BITTER PRINCIPLES.

G. C. JONES.

Aloes, 549; Artemisia Bitters, 550; Hops, 550; Commercial Analysis of Hops, 554.

## ANIMAL BASES.

K. GEORGE FALK.

Ninhydrin Test, 560; van Slyke Apparatus, 560; Sørensen's Method, 561; Esterification Method, 561; Amino-acid Picrolonates, 562; Separation of *d*-Valine and *d*-Alanine, 562; Separation of Cystine and Tyrosine, 563; Tyrosine, 563; Tryptophane, 563; Betaine, 563; Urea, 564; Creatine, 565; Adenine, 568.

## ANIMAL ACIDS.

PHILIP B. HAWK.

Kynurenic Acid, 569; Homogentisic Acid, 569; Hippuric Acid, 569; Uric Acid, 570; Benzoic Acid, 574; Oxalic Acid, 574; Chondroitin-sulphuric Acid, 574; Colloidal Nitrogen, 575; Glycuronic Acid, 575; Amino-acids, 575; Acetone, 576; Aceto-acetic Acid, 577;  $\beta$ -Hydroxybutyric Acid, 578; Bile Acids, 578; Bile Pigments, 579; Urinary Calculi, 580; Hydrochloric Acid, 580.

## LACTIC ACID.

W. A. DAVIS.

Qualitative Tests, 582; British Pharmacopœia, 1914, 582; Estimation of



Lactic Acid in Organic Tissues and Extracts in Presence of  $\beta$ -Hydroxybutyric Acid, 582; Estimation of Lactic Acid in Urine, 584.

### CYANOGEN AND ITS DERIVATIVES.

HERBERT PHILIPP.

Hydrocyanic Acid and Simple Cyanides, 585; Double Cyanides, 587; Compounds of Cyanogen and Iron, 587; Carbonyl Ferrocyanides, 588; Thiocyanates, Sulphocyanides, 589; Cyanamide, 589.

### ENZYMES, 591.

E. FRANKLAND ARMSTRONG.

### PROTEINS.

S. B. SCHRYVA.

Estimation of Espartic and Glutamic Acids in the Products of Protein Hydrolysis, 592.

### VEGETABLE PROTEINS—FLOUR, 593.

E. FRANKLAND ARMSTRONG.

### PROTEINS OF MILK.

L. L. VAN SLYKE.

Method of Preparing Ash-free Casein, 595; Compounds of Casein and Paracasein with Bases, 595; Molecular Weights and Valency of Casein and Paracasein, 596; Estimation of Casein, 596.

### MILK PRODUCTS.

CECIL REVIS AND E. RICHARDS BOLTON.

Regulations in England, Local Government Board, 1912, 597; Regulations as to Preservatives in Food made by Canadian Order-in-Council, April 4, 1914, 597; Estimation of Sugars in Condensed Milk, 597; Aldehyde Figure for Cream, 599; Gerber Method, 599; Analysis of Dried Milks, 600; Analysis of Cheese, 600; Fat Estimation, 600; The Ratzliff-Schmid-Bondzynski Method, 600; Polenske Method, 600; Estimation of Water, 601; Estimation of Fat, 601.

ALBUMINOIDS.

JEROME ALEXANDER.

Albuminoids, 604; Detection of Gelatin, 605.

MEAT AND MEAT PRODUCTS.

JOHN PHILLIPS STREET.

Muscle Extractives, 607; Nitrogenous Muscle Extractives, 609; Estimation of Nitrogenous Extractives, 610; Phosphorous Compounds, 611; Tin in Canned Foods, 612; Decomposition of Meat, 612; Estimation of Ammonia, 612; Frozen Meat, 613; Meat Extracts, 613; Partition of Nitrogen in Meat Extracts, 615; Bouillon Cubes, 616; Soups, 618; Sausage, 619; Composition of Meat Rations, 619; Eggs, 620; Fish, 621.

FIBROIDS.

W. P. DREAPER.

Estimation of Small Quantities of Wool in Cotton Materials, 623.

APPENDIX.

Sugars, 625; Butter, 625; Arginine, 625; Meat Extracts, 625.

INDEX TO VOL. IX . . . . .	627-633
AUTHORS INDEX TO SERIES . . . . .	635-727
SUBJECT INDEX TO SERIES. . . . .	729-836

# ALCOHOLS.

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By G. C. JONES, F. I. C., A. C. G. I.

## METHYL ALCOHOL.

### Detection and Estimation of Methyl Alcohol in Presence of Ethyl Alcohol.

—Since Vol. I appeared, many new methods have been described for this purpose, but, so far as the writer is aware, only one of them marks a real advance. By this method, due originally to Denigès,<sup>1</sup> the presence of 0.2% of methyl alcohol (or about 4% of industrial spirit) in ethyl alcohol can be detected with certainty within 20 minutes, and only twice as much time is required to estimate the proportion of methyl alcohol with sufficient exactness for most purposes. Denigès claims that the method will detect as little as 0.1% of methyl alcohol in ethyl alcohol, and Simmonds<sup>2</sup> has shown that it can be made even more sensitive. The writer's own experience confirms this, but it will be seen from a subsequent paragraph that there is risk in attempting to push the sensitiveness too far, and the method as now to be described will not detect much less than 0.2% of methyl alcohol expressed as a percentage of the total alcohols. This is sensitive enough for almost any purpose, as the addition of less than 5% of industrial spirit to ethyl alcohol would probably represent too small a saving to the sophisticator to be worth his while. The subsequent notes show the direction in which the test should be modified to increase its sensitiveness, should this be necessary.

Simmonds (*loc. cit.*) describes the test as follows: "The alcoholic liquid is first purified, where necessary, either by the method of Thorpe and Holmes (Vol. I, p. 129) or by other suitable means. It is then diluted with water until it contains 10% of total alcohol by volume.

"To 5 c.c. of this prepared liquid, contained in a wide test-tube, are added 2.5 c.c. of permanganate solution (2%), and then 0.2 c.c. of strong sulphuric acid. When the reaction has proceeded for 3 minutes, 0.5 c.c. of oxalic solution (9.6 grm. crystals in 100 c.c.) is added. On shaking, the liquid becomes clear and nearly colourless. 1 c.c. of strong sulphuric acid is now run in and well mixed with the solution, which is finally treated with 5 c.c. of Schiff's reagent. A violet colour is developed in the course of a few minutes unless mere traces of methyl alcohol were present, when 20 or 30 minutes may be required.

<sup>1</sup> *Compt. rend.*, 1910, 150, 832.

<sup>2</sup> *Analyst*, 1912, 37, 16.

"A preliminary experiment carried out as described serves to detect the presence of methyl alcohol and to give some idea of the quantity. According to the indications thus obtained, another part of the prepared liquid is further diluted, if necessary, with ethyl alcohol of 10% strength until it contains from 0.001 to 0.004 grm. methyl alcohol in 5 c.c., and the experiment is repeated side by side with two or more standards for comparison. These contain 0.001, 0.002, 0.003, etc., grm. methyl alcohol in 5 c.c. of 10% ethyl alcohol."

The above description of the test requires so little amplification that the writer has preferred to leave it in the words of Simmonds, who first sought to establish the test here. Simmonds does not give the formula of the Schiff's solution to be used, nor does he, in the writer's view, lay sufficient stress on the necessity of measuring all the reagents used, a point of great importance. Curiously enough, the strength of the oxalic acid, which is of least importance, he states with great precision. He points out, it is true, that the function of the sulphuric acid added immediately before the Schiff's reagent is to suppress any colouration due to acetaldehyde, but does not say that the intensity of colouration due to a stated amount of formaldehyde is closely dependent on the final concentration of acid, as it actually is. Again, the amount of formaldehyde formed from methyl alcohol depends on the exact conditions of oxidation, and even ethyl alcohol itself may yield formaldehyde if the conditions are not strictly controlled. This last fact has settled the fate of many similar methods. In first describing this test Denigès pointed out that the use of too high a concentration of sulphuric acid with the permanganate would give rise to formaldehyde, even with pure ethyl alcohol.

The formula adopted in the preparation of the Schiff's solution is important, as it affects the final concentration of acid. The first (strongly acid) solution described on page 197 of Vol. I is quite useless for the purpose, as are many less acid ones, *e.g.*, that of Mohler,<sup>1</sup> perhaps that most used in the examination of potable spirits. The other solution described in Vol. I, made from magenta base and sulphurous acid, serves well and was used in all the experiments described below.

A 9.6% solution of oxalic acid, as recommended by Simmonds, deposits crystals at ordinary temperatures, but with a cold saturated solution of oxalic acid, Schiff's solution of the character recommended above, and precise measurement of quantities, Simmonds' directions may be followed.

How nearly the quantities need to be measured and how they should be varied to increase or diminish the sensitiveness of the test will be evident from the following results obtained in the writer's laboratory.

The amount of permanganate used must be rigidly adhered to in quantitative work, since it determines the amount of formaldehyde formed and the final intensity of colour. The use of 2 c.c. in place of 2.5 c.c. reduces the final

<sup>1</sup> Frémy's *Encyclopédie Chimique*, 1892, X, 11, 278.

colour about 30%, whilst the use of 5 c.c. more than doubles the sensitiveness of the test, when all other conditions are kept the same, except that the use of 5 c.c. of permanganate necessitates the subsequent use of about 1 c.c. instead of 0.5 c.c. of oxalic acid solution. Provided all the other standard conditions are rigidly adhered to, this is the simplest and safest way of increasing the sensitiveness of the test, as ethyl alcohol under these conditions yields no formaldehyde and no colour, but the permissible latitude in all the other measurements necessarily becomes narrower.

The amount of sulphuric acid added with the permanganate is less important. The amount of formaldehyde produced is greater with more acid, but, within the limits 0.1–0.3 c.c., the final results are indistinguishable, owing to the compensating effect of the higher final concentration of acid reducing the intensity of colour due to a definite quantity of formaldehyde. Quantities in excess of 0.5 c.c., however, might lead to formaldehyde being produced from ethyl alcohol itself.

The time allowed for oxidation, provided it be not less than 3 minutes, appears to be without effect. The influence of temperature may not be negligible, but the point was not investigated, as this would clearly be constant in any one set of experiments.

Not much less than 0.5 c.c. of a cold saturated solution of oxalic acid will reduce the excess of permanganate in the cold, faintly acid solution, but larger quantities, up to 1 c.c., appear to have no appreciable influence on the results.

The subsequent addition of sulphuric acid must be as nearly as possible the same in any one set of experiments and is most conveniently made 1 c.c. as directed by Simmonds. With only 0.6 c.c. added, the acetaldehyde derived from pure ethyl alcohol will give a distinct colouration with Schiff's solution of the character described. With 0.75 c.c. or more, pure ethyl alcohol gives no purple or even blue colour, provided all the other standard conditions are rigidly adhered to, but it is unwise to reduce the amount below 1 c.c. except in very special circumstances, when it is necessary to make the test as sensitive as possible. In such cases, the sensitiveness of the test can be increased about 40% by using only 0.75 c.c. of acid, but very careful control experiments then become necessary. On the other hand, not more than 1 c.c. of acid should be used, as the use of so much as 1.25 c.c. reduces the sensitiveness of the test by about 30%, whilst 1.5 c.c. reduces it 50% and 2 c.c. nearly 90%.

Finally, the amount of Schiff's solution taken is not without influence. If 10 c.c. be taken instead of 5 c.c., the concentration of acid is so much reduced that even the acetaldehyde from ethyl alcohol develops a colour. On the other hand, the use of only 2 c.c. in place of 5 c.c. reduces by about 90% the amount of colour developed by a fixed quantity of formaldehyde.<sup>1</sup>

<sup>1</sup> *Analyst*, 1915, 40, 218.

## ETHYL ALCOHOL.

**Estimation of Alcohol by the Ebullioscopic Method.**—This method (Vol. I, p. 126) has been considerably developed of late, especially in France, where it is used for official purposes. The latest form of apparatus, a proprietary design, is costly, but it gives results of great exactness, and is operated simply; consequently it may be expected to find increasing use in laboratories where large numbers of alcohol estimations must be made. It has been described by J. C. Cain.<sup>1</sup>

## ERRATA, VOL. I.

Page 14. In the tables of sp. gr. corresponding with degrees Baumé given by the United States Dept. of Agriculture Bull., No. 107 (Revised, 1912), pp. 221-224, which are based on the work of Matejczek and Scheibler (*Zeit. Ver. Deuts. Zuckerind.*, 1865, 15, 580; 1874, 24, 827), the degrees Baumé are on the "old" Rational Scale of Kolb, and refer to 17.5° C. On page 292 of Vol. I the values given are Baumé degrees on the Gerlach scale at 17.5°,  $\text{sp. gr.} = \frac{146.8}{146.8 - \pi}$  at 17.5°.

Page 15, line 15 from bottom, "in the other cases" should read "in other cases."

Page 17, line 15 from bottom, "is destroyed" should read "disappears."

Page 20, line 13 "577.9" should read "757.9."

Page 26, line 10 from bottom "Fig. 12" should be "Fig. 13."

Page 29, lines 4, 9 and 11 from bottom, for "C" read "L"; line 7 from bottom, for "tube D" read "vessel B."

Page 33, line 9, for "Fig. 12" read "Fig. 13."

Page 39, line 8, for "Vol. II" read "Vol. III."

Page 44, line 7 from bottom; for "is" read "in."

Page 46, line 3, for "in" read "on."

Page 48, line 8 from bottom, for "quire" read "quite."

Page 55, line 17 from bottom, for "Vol. II" read "Vol. III."

Page 56 line 5 from bottom, for "comyany" read "Company."

Page 59, line 11 from bottom, for "is not well adapted to" read "unsuitable for."

Page 86, line 12, for "met, hyl" read "methyl."

Page 92, line 11, for "Ester," read "Esters."

Page 94, line 1, for  $\text{H}_2\text{CrO}_4$  read  $\text{CrO}_3$ .

Page 96, line 13, for semicolon put comma and line 14, after reached, insert semicolon.

Page 98, line 16, insert comma after "respectively"; line 23, after carbonate insert "are" line 10 from bottom, for "rodium" read "sodium."

Page 105, lines 17 and 18 from bottom should be transposed.

Page 108, lines 16 and 17 from bottom should be transposed.

Page 109, lines 8 and 9 should be transposed.

Page 110, line 15 from bottom, for "which alcohol has" read "whose alcohol had."

Page 129, line 2 from bottom, for "one" read "a single."

Page 129, bottom line, for "extraction spirit" read "extraction with petroleum spirit."

<sup>1</sup> *Chem. News*, 1914, 109, 37.

# MALT AND BREWING MATERIALS.

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BY G. C. JONES, F. I. C., A. C. G. I.

## MALT.

**Extract.**—On page 134 of Vol. I, directions are given to grind malt in a “Seck” mill set at  $25^{\circ}$  on the arbitrary scale attached to that instrument. It has been found that Seck mills, although sold as standard instruments at a very high price, differ widely amongst themselves. Since, however, large numbers have been installed in brewing laboratories, it has been decided by the Malt Analysis Committee of the Institute of Brewing<sup>1</sup> to continue their use for the present but, instead of relying on the arbitrary scale, to set each mill so that the rollers are 0.5 mm. apart, as determined by a feeler gauge.

**Diastatic Power.**—The most frequent cause of divergence between the results of different workers is the use of starch solutions of different degrees of acidity. There are other, less easily avoidable sources of error (cf. *J. Inst. Brewing*, 1908, 14, 12), but this one is readily avoided. The 2% starch solution should on no account be alkaline when tested hot with alizarin, nor should it be so strongly acid that 200 c.c. require more than 0.2 c.c. of decinormal caustic alkali to neutralise it. Two drops of a suspension (1 : 200) of alizarin paste confer a scarcely perceptible yellow tint on the acid or “neutral” solution, but the change to incipient purple on adding the least excess of alkali is quite sharp.

The temperature at which the 5% malt extract is made may be  $70 \pm 5^{\circ}$  F. without influence on the results, but the temperature of the starch digestion must be precisely  $70^{\circ}$  and the time precisely 1 hour. An error here of  $1^{\circ}$  or  $2'$  introduces an error of about 3% in the results.

Ferrous thiocyanate is not obtainable commercially and, if it were, would almost certainly be contaminated with ferric salts. The indicator referred to in Vol. I is made as follows:

One grm. of ferrous ammonium sulphate is dissolved in 10 c.c. of cold water, 1.5 grm. of ammonium thiocyanate is added and, when this has dissolved, 2.5 c.c. of concentrated hydrochloric acid. With the purest available materials, the solution, even when freshly prepared, will usually have a pink tint. This is destroyed by a trace of zinc dust and the solution is filtered. After being kept some time, it re-acquires a red colour, which is again discharged by the use of zinc dust. In this way the indicator may be used for

<sup>1</sup> *J. Inst. Brewing*, 1910, 16, 531.



several days, but finally becomes too insensitive and must be replaced by a freshly prepared solution.

### Roasted Malt and Barley.

A uniform practice in analysing these products has now been agreed on<sup>1</sup> which differs considerably from the methods described in Vol. I (p. 142).

**Extract.**—A little over 50 grm. is finely ground in a coffee mill, and exactly 50 grm. of the ground product are mixed with about 350 c.c. of boiling distilled water and the mixture kept in a boiling water bath for an hour. It is then cooled, made up to 515 c.c., filtered and its sp. gr. at 60°/60° taken. The excess gravity (over water = 1,000) multiplied by 3.36 gives the extract in brewers' lb. per standard quarter of 336 lb. Black barleys and malts are not commonly purchased on the basis of the standard quarter of 336 lb., various weights and measures being employed, but the Malt Analysis Committee of the Institute of Brewing recommends the above uniform method of stating analytical results, leaving subsequent calculation to whom it may concern.

**Colour.**—20 c.c. of the above extract, which, if not brilliant, must be re-filtered, are diluted to 1,000 c.c. and the colour read in a 1-in. cell, using Lovibond's tintometer and glasses of "Series 52."

### Brown and Crystal Malts.

No directions for the analysis of these materials were given in Vol. I. The following uniform methods have now been agreed on.<sup>2</sup>

**Extract.**—50 grm. are ground in a Seck mill, so set that there is a distance of 0.5 mm. between the rollers, as determined by a feeler gauge. The grist is mashed with 300 c.c. of distilled water at 158° F. and 100 c.c. of cold-water malt extract<sup>3</sup> previously heated to 150° F. The mixture is kept for an hour at 150° F., then cooled to 60° F., made up to 515 c.c., filtered and the sp. gr. of the filtrate taken at 60°/60° F. Simultaneously, 100 c.c. of the cold-water malt extract, mixed with 300 c.c. water, are digested for an hour at 150° F., then cooled to 60° F., made up to 500 c.c., filtered and the sp. gr. of the filtrate taken. The difference between the sp. gr. (water = 1,000) of this filtrate and that obtained in the experiment with brown or crystal malt, multiplied by 3.36, gives the extract of the malt in brewers' lb. per standard quarter of 336 lb. Brown and crystal malts are not commonly purchased on the basis of the standard quarter, various weights and measures being employed, but the above uniform method of stating results is recommended.

<sup>1</sup> *J. Inst. Brewing*, 1910, 16, 532.

<sup>2</sup> *J. Inst. Brewing*, 1910, 16, 532.

<sup>3</sup> The cold-water malt extract is made by digesting malt of diastatic power 30 to 40° Lintner with three times its weight of distilled water for 1 hour at 60°–70° F., and then filtering.

**Colour.**—20 c.c. of the above extract, which must be brilliant, are diluted to 100 c.c. and the colour read in a 1-in. cell, using a Lovibond tintometer and glasses of "Series 52."

### Caramel.

**Extract.**—10 grm. are dissolved in distilled water, made up to 100 c.c., filtered and the sp. gr. of the filtrate determined at 60°/60° F. The excess gravity (water = 1000) multiplied by 2.24 gives the extract in brewers' lb. per 2 cwt.

**Colour.**—10 c.c. of the above solution are diluted to 1,000 c.c., and the colour read in a 1-in. cell, using a Lovibond tintometer and glasses of "Series 52."

**Ash.**—3 grm. are treated with 2 c.c. of sulphuric acid in a tared dish, which is then heated over a flame until intumescence is complete, when it is transferred to a muffle and the contents are incinerated at a low red heat. It is usual to deduct 10% from the weight of the ash found, as in the analysis of sugars, though the mineral constituents of caramel are so frequently mainly sulphates that no correction, or at most a very small one, is really needed.

Iron is nearly always present in detectable amount and, since brewers object to more than a minute trace of iron in their materials, it is usual to estimate the iron in the ash by dissolving the latter in hydrochloric acid, adding much thiocyanate and comparing the colour produced with standards containing known amounts of ferric iron and the same concentration of acid and thiocyanate.

Caramel for use in brewing should throw down no sediment when mixed with beer. The test is usually continued for 24 hours. If prolonged beyond this period, as is sometimes worth while, some beer without caramel should be set up alongside, lest a sediment due to the beer itself be attributed to the caramel.

### Invert Sugar.

Invert sugar, made by hydrolysing raw cane sugars with acid, is an important brewing material and is subjected in brewing laboratories to a much more exhaustive scheme of analysis than is to be found under this heading in the section on Sugars.

Invert sugar made from refined sugar lacks the lusciousness and other characteristics desirable in a brewing sugar, so that raw cane sugars are generally used. In addition to invert sugar, uninverted saccharose and water, therefore, commercial invert contains from 0.2 to 0.7% of albuminoids, from 3 to 6% of unfermentable organic matter and from 1 to 3.5% of mineral matter, the latter being partly derived from the raw material and partly introduced as calcium carbonate to neutralise the acid used in effecting

hydrolysis. Sulphuric acid is generally employed as hydrolyst because the comparative insolubility of calcium sulphate makes it possible to eliminate most of the mineral matter introduced for the purpose of neutralisation.

Raw beet sugar could not be used for the production of brewers' invert, on account of the objectionable flavour of the secondary constituents. No such objection would attach to the use of highly refined beet sugar, but highly refined sugars are not used for the reasons already stated. Occasionally invert sugar is made from a mixture of raw cane sugar and high-grade raw beet sugars (first runnings) and the origin of such invert sugar is not readily detected by the palate or nose. It is, however, desirable to exclude it from the brewery, and this can usually be done by limiting the permissible percentage of albuminoids, which is higher in beet than in cane products. Brewers' invert is supplied in three grades, and it is reasonable to require them to contain less than the following percentages of albuminoids: No. I, 0.3%; No. II, 0.5%; and No. III, 0.75%. A good No. III will comply with the standard here set up for No. I, so that the above limits cannot be unduly stringent.<sup>1</sup>

The analysis of commercial invert includes the following determinations: dextrose, lævulose, saccharose, albuminoids, ash and water. The difference between the sum of these and 100 is returned as "other organic matter." The brewers' extract per 2 cwt. is also an important figure, always determined, and the colour may be.

**Ash.**—This is determined as in caramel (*q.v.*) and it is customary to deduct 10% from the weight of the sulphated ash as with other sugars, although the correction is no doubt too large for a product inverted with sulphuric acid.

**Water and Brewers' Extract.**—25 gm. are dissolved in distilled water, the mixture made up to 250 c.c., filtered, and its sp. gr. determined at 60°/60°. The excess gravity (water = 1,000) multiplied by 2.24 gives the extract in brewers' lb. per 2 cwt.

**Water.**—A 10% solution of pure invert sugar has a sp. gr. of 1,038.7 and, in solutions of approximately this concentration, the excess sp. gr. is very nearly proportional to the concentration. The composition of a solution of pure invert sugar can therefore be calculated by dividing the excess gravity by the "solution factor" 3.87. The solution factor of uninverted sucrose is 3.86, and that of the other organic solids of commercial invert probably not very different, whilst their amount is small. The solution factor of the ash constituents, on the other hand, approximates to 8 and in brewery laboratories is usually assumed to be double that of the organic solids. The percentage of total solids in the invert is therefore arrived at by dividing the excess gravity of the 10% solution by 0.387 and subtracting the percentage of ash. The difference between the result so found and 100 is the percentage of water in the sample.

<sup>1</sup> cf. Ling, *J. Inst. Brewing*, 1914, 20, 185.

**Albuminoids.**—Nitrogen is determined by Kjeldahl's method and the result multiplied by 6.3. If unduly high, a separate determination of nitrate nitrogen should be made before condemning the sample on its high content of "albuminoids."

**Invert Sugar and Saccharose.**—These can be estimated by a method, worked out by Morris<sup>1</sup> who first devised a means of overcoming the interference of optically active and reducing non-sugars. The following method, based on that of Morris, is easier of execution and has been found by Ling (its originator) and the writer to be capable of a somewhat higher degree of accuracy. It depends on the volumetric estimation of the reducing sugars and the use of the table constructed by Ling and the writer.<sup>2</sup> The table was constructed from experiments made with Fehling's solution of which 10 c.c. required 25.65 c.c. of 0.2% pure invert sugar. If another worker finds that 10 c.c. of his Fehling's solution requires under his conditions only 25 c.c. of 0.2% invert sugar, he will need to reduce the numbers in columns D, L, I and M and increase those in columns D', L', I' and M' proportionately. The maltose columns are for use in the analysis of commercial glucose (*vide supra*).

To make clear the calculations involved, the following description of the method is accompanied by a worked example.

The rotation of the 10% solution, prepared for the estimation of water and brewers' extract, is observed in a 200 mm. tube in a Ventzke-Scheibler half-shadow polarimeter. 10 c.c. of this solution are diluted to 500 c.c. and the reducing power of this 0.2% solution determined by titration with 10-c.c. portions of Fehling's solution, using ferrous thiocyanate as indicator (cf. Vol. I, p. 136, for method, and this Vol., p. 5, for preparation of indicator).

In a particular case, a commercial invert sugar gave a reading in 10% solution in a 200-mm. tube of  $-4.7$  divisions, and 10 c.c. of Fehling's solution required 36.45 c.c. of 0.2% solution for reduction.

10 c.c. of the 10% solution are diluted to about 150 c.c. and boiled for 1 minute with 30 c.c. of  $N/2$  hydrochloric acid to invert the small amount of saccharose always present in commercial invert sugar. The mixture is cooled, neutralised with 30 c.c. of  $N/2$  sodium hydroxide, diluted to 500 c.c. and titrated against Fehling's solution.

In the case cited, 10 c.c. of Fehling's solution required 35.95 c.c. of the completely inverted 0.2% solution. From this result and the reducing power of the 0.2% solution before inversion, the percentage of Saccharose is calculated. Reference to column 1 of the table shows that the reducing power of the inverted solution corresponds to the presence of 0.1460% of apparent invert sugar, that of the uninverted solution to 0.1441%. The difference, 0.0019, is the measure, in terms of invert sugar, of the saccharose

<sup>1</sup> *J. Inst. Brewing*, 1898, 4, 162.

<sup>2</sup> *Analyst*, 1908, 33, 160. (See under Sugars, page 39.)

in 0.2 gm. of the sample, which therefore contained  $(0.0019 \times 0.95 \times 500 =)$  0.9% saccharose.

25 gm. of the original sample are dissolved in about 200 c.c. water, to which about 5 c.c. of yeast decoction and 3 gm. of washed, pressed yeast are added, and the mixture is allowed to ferment at about 70° C. for 3-4 days. A little alumina cream is then added, the mixture made up to 250 c.c., filtered and its rotation and reducing power determined.

In the case cited, the fermented 10% solution gave a reading in a 200 mm. tube of -0.1 division, and 40 c.c. was required to reduce 10 c.c. of Fehling's solution. Opposite 40 c.c. in column I of the table is the number 0.1319, the reducing power in terms of invert of the unfermentable matter in 10% solution. In 0.2% solution, therefore, the unfermentable matter would raise the apparent content of invert sugar 0.0026%. The table also shows that in a concentration such that 10 c.c. Fehling's solution require 36-37 c.c., a difference of 0.0037% of invert sugar makes a difference of 1 c.c. in the burette reading. Unfermentable reducing substances equivalent to 0.0026% invert would therefore reduce it 0.70 c.c. 10 c.c. of Fehling's solution would therefore require  $(36.45 + 0.70 =)$  37.15 c.c. of the 0.2% solution, if this were free from unfermentable reducing substances, or 1 gm. of the sample contains dextrose and lævulose equivalent to  $10 \div (37.15 \times 0.002) = 10 \div 0.0743 = 134.6$  c.c. Fehling's solution.

In concentrations such as that in which the first reduction experiment was made—namely where 10 c.c. Fehling's solution require 36.45 c.c. of sugar solution—1 gm. dextrose = 196.6 c.c. Fehling's solution and 1 gm. lævulose = 183.8 c.c. Fehling's solution. If the percentage of dextrose in the sample be represented by D and the percentage of lævulose by L, it follows that

$$1.966 D + 1.838 L = 134.6 \quad (1)$$

The sample was found to contain 0.9% saccharose. A 0.9% solution of saccharose gives a reading of  $(3.85 \times 0.09 =)$  + 0.3 division when read in a 200-mm. tube in a Ventzke-Scheibler polarimeter. The actual reading (-4.7 must therefore be corrected for this amount, as well as for the reading of the unfermentable residue (-0.1), in order to arrive at the reading due to dextrose and lævulose alone,  $-4.7 - 0.3 - (-0.1) = -4.9$  divisions. Since 1% solutions of dextrose or lævulose give readings of 3.05 and -5.32 divisions respectively, it follows that

$$0.305 D - 0.532 L = -4.9 \quad (2)$$

From equations (1) and (2),  $D = 39.0$  and  $L = 31.5\%$ .

### Starch Sugars.

Glucose chips contain in addition to dextrose, maltose (nil to 12%), dextrin (up to 14%), water (usually 13-14%), small amounts of mineral

matter (0.5–2%) and still smaller amounts of albuminoids (0.2–0.6%). Glucose syrup or dextrin-maltose usually contains rather less than 25% of dextrose, rather more maltose,<sup>1</sup> over 30% of dextrin, about 18% of water and traces of mineral matter and albuminoids.

As regards ash, albuminoids, water and brewers' extract, these sugars are analysed like commercial invert sugar (*q.v.*).

Dextrose and maltose are estimated in a manner similar to that employed for the estimation of dextrose and lævulose in invert sugar, except that no inversion experiment is necessary and that the equations to be used are:

$$\begin{aligned} aD + 1.225M &= F, & (1) \\ 0.305D + 0.798M &= R, & (2) \end{aligned}$$

where  $a$  is a coefficient found by reference to the table on page 39 after experiment, as in the analysis of invert sugar,  $F$  is the number of c.c. of Fehling's solution corresponding to 1 grm. of the starch sugar, duly corrected for the reducing power of the unfermentable residue, and  $R$  is the rotation in divisions Ventzke (200 mm. tube) of a 10% solution of the sugar, duly corrected for the rotatory power of the unfermentable residue. The coefficient of  $M$  in equation (1) is a constant, independent of the concentration.

The difference between 100 and the sum of the percentages of dextrose, maltose, water, ash and albuminoids may be, and usually is, returned as "dextrinous carbohydrates and other organic matter." The percentage of actual dextrin is approximately given by dividing the rotation (Ventzke, 200 mm. tube) of the fermented 10% solution by 1.166.

### Beer.

**Determination of Original Gravity.**—The Finance Act of 1914 (Session 2) substitutes for the table, reproduced on page 153 of Vol. I, a new table, of which a copy is given below.

The figures in the new table, which is based on experiments made *ad hoc* by Sir Edward Thorpe and Dr. Horace Brown, are for the most part higher—and, over an important part of the table, nearly 2° higher—than those in the old one, which has long been known to give low results (cf. Vol. I, 155). On the average, the new table will allow original gravities to be determined accurately, but in some cases it will overestimate and in others underestimate original gravities. This is inevitable, as the true relation between spirit indication and degrees of gravity lost varies with the composition of the wort and with the individual brewery. To meet cases where it may overestimate, the Finance Act directs that 0.75° be deducted in all cases from the original gravity as deduced from the table. This, of course,

<sup>1</sup> Kluyver (*Biochemische Suikerbepalingen*, Leiden, 1914) states that a series of analyses, made by discriminating yeasts, of commercial glucose syrups showed the presence of 15 to 20% of maltose in the products he examined. W. A. D.

applies to work connected with the departments of Customs and Excise. For purposes of brewery control, it may be found that a smaller correction, or one of contrary sign, or none, is needed.

SPIRIT INDICATION TABLE SHOWING DEGREES OF GRAVITY LOST IN MALT WORT DURING FERMENTATION.

Degrees of spirit indication	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.00	0.42	0.85	1.27	1.70	2.12	2.55	2.97	3.40	3.82
1	4.25	4.67	5.10	5.52	5.95	6.37	6.80	7.22	7.65	8.07
2	8.50	8.94	9.38	9.82	10.26	10.70	11.14	11.58	12.02	12.46
3	12.90	13.34	13.78	14.22	14.66	15.10	15.54	15.98	16.42	16.86
4	17.30	17.75	18.21	18.66	19.12	19.57	20.03	20.48	20.94	21.39
5	21.85	22.30	22.76	23.21	23.67	24.12	24.58	25.03	25.49	25.94
6	26.40	26.86	27.32	27.78	28.24	28.70	29.16	29.62	30.08	30.54
7	31.00	31.46	31.93	32.39	32.86	33.32	33.79	34.25	34.72	35.18
8	35.65	36.11	36.58	37.04	37.51	37.97	38.44	38.90	39.37	39.83
9	40.30	40.77	41.24	41.71	42.18	42.65	43.12	43.59	44.06	44.53
10	45.00	45.48	45.97	46.45	46.94	47.42	47.91	48.39	48.88	49.36
11	49.85	50.35	50.85	51.35	51.85	52.35	52.85	53.35	53.85	54.35
12	54.85	55.36	55.87	56.38	56.89	57.40	57.91	58.42	58.93	59.44
13	59.95	60.46	60.97	61.48	61.99	62.51	63.01	63.52	64.03	64.54
14	65.10	65.62	66.14	66.66	67.18	67.70	68.22	68.74	69.26	69.78
15	70.30	70.83	71.36	71.89	72.42	72.95	73.48	74.01	74.54	75.07
16	75.60	.....	.....	.....	.....	.....	.....	.....	.....	.....

ERRATA IN VOL. I.

Page 161, line 15, for "hopsarrogates," read "hop surrogates," 164, line 13, for "saccharine," read "saccharin."



# WINES AND SPIRITS.

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By G. C. JONES, F. I. C., A. C. G. I.

**Physico-chemical Analysis of Wines.**—The time has not yet come for the description, in a general work like this, of the physico-chemical methods of P. Dutoit and M. Duboux. Nothing less than a detailed description, occupying much space, could serve any useful purpose, and this would scarcely be justified, seeing that the methods are not yet used in this country, so far as the writer is aware, whilst they are ignored by all German writers, *e.g.*, by the author of the section on Wines in the most recent edition of Lunge's *Technical Methods of Analysis*.

However, the application by Dutoit and Duboux of their methods to the investigation of wine dates back at least to 1908 and is of general interest, if only for its originality. It is quite probable that the methods may come into general use in laboratories where a large amount of routine work has to be conducted. Such work on wine is not often undertaken in Great Britain, but those who refer to this book have a right to expect at least a reference to work which may become important before another edition appears. Fortunately, the authors have recently published a small book,<sup>1</sup> which makes it unnecessary to give references to their original papers, some of which appeared in Swiss periodicals, not readily accessible.

Briefly, their methods consist in titrating the wine with appropriate reagents and taking successive conductivity measurements, the results being plotted on a system of rectangular coordinates. In this way, curves are obtained which show distinctly the saturation points. Not only can chlorides, sulphates, phosphates, lime, total alkalinity, total acidity, ash and ammonia be thus estimated, but also tartaric, malic and succinic acids.

The book referred to embodies their work up to 1912, since when only one paper has been published.

**Estimation of Tartaric, Malic, Succinic and Other Organic Acids in Wine.**—The estimation of tartaric acid and tartrates so seldom figures in an English report on a wine that a mere reference to the tedious methods of Halenke and Moslinger was given in Vol. I. For the same reason, no extended reference can be given here to improved methods for the estimation of tartaric, malic and other acids in musts, wines and the like. But the last 5 years have witnessed several more or less successful attempts to solve the difficult problem of estimating these acids when present together; for these methods, see under Tartaric Acid, pages 104–109.

<sup>1</sup> *L'Analyse des Vins par Volumetrie Physico-Chimique.* Lausanne, Rouge et Cie.



## ERRATA IN VOL. I.

- Page 165, line 2, for A. C. S. I. read "A. C. G. I."  
Page 165, line 21, from bottom, for "difference," read "differences."  
Page 168, line 13, after "wines" insert "in which."  
Page 174, line 18, insert "acid" after "sulphurous."  
Page 175, line 20 from bottom, for Vol. III, read Vol. V.  
Page 175, line 8 from bottom, for "forms," read "form."  
Page 191, line 8 from bottom, for "bearing," read "leaving."  
Page 196, line 8, for "in," read "under."  
Page 205, line 2, for "Schlighting," read "Schlichting."

# YEAST.

By EMIL SCHLICHTING AND H. WINTHER.

**General.**—Yeast must be considered from two points of view, as a plant and as a ferment, based upon the fact that, while the yeast cells develop and propagate, the yeast has only little or no fermentative activity.

**Physical Properties.**—According to Schönfeld, Hinrichs and Rossmann,<sup>1</sup> the four main characteristics of a “*top fermenting yeast*” are: (1) branched budding fermentation; (2) little fermentation of melitriose; (3) formation of surface yeast at room temperature; (4) milky mixture in water.

Schönfeld and Hirt<sup>2</sup> point out that considerable difference exists among the various yeasts in their mode of settling or sedimentation, some separating out in heavy lumps while others subside as a fine, loose dust. According to these authors, lumpy yeasts contain a larger percentage of phosphoric acid and magnesia. The distinctive character of settling is also greatly influenced by the nature of the proteins contained in the nutritive medium. The more complex their molecular composition the greater the tendency of the yeast to separate in solid, lumpy formation.

**Classification.**—In the latest systematizing of yeasts, Hansen<sup>3</sup> distinguishes between the following groups:

*Saccharomyces.*

*Zygosaccharomyces.*

*Saccharomycodes.*

*Saccharomycopsis*

*Pichia.*

*Willia.*

The *Schizosaccharomyces* are not included in this family. Simultaneously with these changes in the grouping of yeasts, several of the known species have been given new names. The most important of these changes are:

Old name.	New name.
<i>Saccharomyces Ellipsoides</i> I.	<i>Saccharomyces Ellipsoides.</i>
<i>Saccharomyces Ellipsoides</i> II.	<i>Saccharomyces Turbidans.</i>
<i>Saccharomyces Pastorianus</i> I.	<i>Saccharomyces Pastorianus.</i>
<i>Saccharomyces Pastorianus</i> II.	<i>Saccharomyces Intermedius.</i>
<i>Saccharomyces Pastorianus</i> III.	<i>Saccharomyces Validus.</i>
<i>Saccharomyces Membranefaciens.</i>	<i>Pichia Membranefaciens.</i>
Carlsberg Yeast I.	<i>Saccharomyces Carlsbergensis.</i>
Carlsberg Yeast II.	<i>Saccharomyces Monacensis.</i>

**Chemical Composition.**—The characteristic odour of yeast is ascribed<sup>4</sup> to a colourless ethereal oil, which, in concentrated form, resembles the flavour of hyacinth.

<sup>1</sup> *Wochenschrift Brau.*, 1910, 27, 493.

<sup>2</sup> *Wochenschrift Brau.*, 1912, 29, p. 174.

<sup>3</sup> P. Lafar, *Techn. Mykologie*, IV, p. 172.

<sup>4</sup> Delbrück, *Brau. Lexikon*, 1910, 455.

Henneberg has found that a definite relation exists between the amount of protein and glycogen present in yeast and that when the former rises above 53%, the latter is reduced to almost nil.

Salkowski<sup>2</sup> has determined the amount of yeast gum to be about 5%. He has further shown that the gum consists of a dextro-mannan, which on hydrolysis forms dextrose and mannose.

**Fermenting Enzyme.**—A. V. Lebedew<sup>3</sup> has demonstrated that the active fermenting enzyme can be extracted from dried yeast by simple maceration with water at a temperature from 25° to 30° C. for a period of 2 hours.

The process of decomposition of sugar into alcohol and carbon dioxide is a very complicated one.<sup>4</sup> According to Harden and Young, the transformation is carried out by the zymase proper and its co-enzyme, which is considered to be an easily saponified ester of phosphoric acid.

The destruction of the activity of pressed yeast juice is mainly ascribed to the action of a saponifying enzyme or lipase upon the co-enzyme; this is also accompanied by the action of a proteolytic enzyme, endotryptase, upon the zymase. Inactive yeast juice may be regenerated by the addition of yeast water if such addition is made shortly after the inactivity has set in.

**Testing of Yeast.**—C. Nagel<sup>5</sup> has modified the Hayduck method of estimating the fermenting power of yeast for baking purposes by changing the composition of the solution employed in the following manner:

400 c.c. of 10% cane-sugar solution to which are added 2 grm. of potassium hydrogen phosphate; 1 grm. of ammonium hydrogen phosphate; 0.25 grm. magnesium sulphate; 0.20 grm. calcium sulphate. The valuation of the yeast is based upon the amount of carbon dioxide generated within 2 hours, and may be expressed as follows:

	Fermenting power.
1000 c.c. of CO <sub>2</sub>	good
800 to 1000 c.c. of CO <sub>2</sub>	medium
less than 800 c.c. of CO <sub>2</sub>	poor

**Dry Yeast.**—According to Hayduck and Bulle,<sup>6</sup> when in the drying process of the yeast proper, the moisture content drops below 25 or 30%, all vegetative cells are killed. That sometimes such yeast will start to grow again, is entirely due to some surviving spores.

In order to produce a dried yeast with about 90% of living cells, it should be mixed with 10% of cane sugar at a temperature of 50° and the mixture should be dried at this temperature on gauze, the period of drying being about 3 hours. The drying may be accelerated by a strong air current; as the sugar added is fermented during the drying process, little or no sugar will be found in the finished product.

<sup>1</sup> *Wochenschrift Bran.*, 1910, 27, 429.

<sup>2</sup> *Chem. Centralbl.*, 1911.

<sup>3</sup> *Annales de l'Institut Pasteur*, 1912, 26, 8.

<sup>4</sup> Delbrück, *Brauerei Lexikon*, 1910, 865.

<sup>5</sup> *Brennerei Zeitung*, 1911.

<sup>6</sup> *Wochenschrift Bran.*, 1912, vol. 29, 489.

The drying of yeast has lately become a general practice especially in Europe for economic reasons and various forms of apparatus have been constructed for this purpose. It has been definitely established that yeast after being freed from its bitter substances is an admirable substitute for meat in the production of extracts, bouillon, etc. The nitrogenous substances in this "*nutrient yeast*" are almost entirely soluble and assimilable. Their nutritive value is very high, approximately three times that of fresh meat.<sup>1</sup>

Hayduck<sup>2</sup> has found that yeast taken from the bottom of a fermented liquid contains an appreciable amount of alcohol, which, under the conditions ordinarily prevailing in breweries, amounts to about 3% of the total yeast. As soon as methods for the separation of this alcohol are perfected, it will constitute an important by-product of the yeast-drying process.

#### ERRATA IN VOL. I.

Page 205, "E. Schlighting" should be "E. Schlichting. 12th line "thoughtout" should "be throughout."

Page 207, 9th line, "bodies or peptones" should be "bodies such as peptones."

<sup>1</sup>Hayduck, *Jaabuch Vers. und Lehranst. Brau.*, 1911, 286.

<sup>2</sup>*Jahrb. Vers. Lehranst. Brau.*, 1913, 536.

## NEUTRAL ALCOHOLIC DERIVATIVES.

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For a comprehensive review of the methods dealing with ether, ethyl chloride and chloroform and of the literature reference should be made as follows:

*Ether.*—Baskerville and Hamor, *J. Ind. Eng. Chem.*, 3, 301-317.

*Ethyl Chloride.*—Baskerville and Hamor, *J. Ind. Eng. Chem.*, 5, 828-831.

*Chloroform.*—Baskerville and Hamor, *J. Ind. Eng. Chem.*, 4, 212-220.

# SUGARS.

By WILLIAM A. DAVIS.

**Solution Densities.**—Probably the most accurate values of the divisors at different concentrations for saccharose, dextrose, lævulose, invert sugar, maltose and “low,” “medium” and “high” starch conversion products are those of Brown, Morris and Millar.<sup>1</sup> These authors give the sp. gr. taken at 15.5° and referred to water at the same temperature; the divisors are not exactly grams per *true* 100 c.c. but the weight of substance (weighed in air) contained in a volume of the solution equal to that occupied by 100 grm. of water at 15.5° weighed in air against brass weights. In order to convert the results into grams per true 100 c.c., when great accuracy is desired, as for instance in determining specific rotatory constants, they must be multiplied by the factor 0.99802, thus reducing them by about 0.2%. The following equations summarise the results; in the original paper the results are also given in the form of tables and curves from which the divisors corresponding with different concentrations can be read directly.

D is the required divisor in grams of anhydrous sugar per 100 c.c. (reputed).

G is the sp. gr. at 15.5° when water at the same temperature = 1,000.

For *Dextrose*,  $D = 3.848 - 0.00028 (G - 1,000) - 0.0000028 (G - 1,000)^2$ .

*Lævulose*,  $D = 3.946 - 0.00068 (G - 1,000) - 0.0000007 (G - 1,000)^2$ .

*Invert Sugar*,  $D = 3.897 - 0.00025 (G - 1,000) - 0.0000004 (G - 1,000)^2$ .

*Maltose*,  $D = 3.9435 - 0.00044 (G - 1,000) - 0.000001 (G - 1,000)^2$ .

“*High Transformation*” of starch by diastase,  $[\alpha]_D 188.6^\circ$ ,  $R = 20.2$ .

$D = 4.032 - 0.0006 (G - 1,000)$ .

“*Low Transformation*” of starch,  $[\alpha]_D 149.7^\circ$ .  $R = 82.8$ .

$D = 3.9742 - 0.000403 (G - 1,000) - 0.0000014 (G - 1,000)^2$ .

Ling, Eynon and Lane<sup>2</sup> have since re-determined the solution densities of dextrose, lævulose and maltose, for concentrations ranging from  $c = 1$  to  $c = 24$ . The results practically confirm those of Brown, Morris and Millar and are of importance because special care was taken to ensure the purity of the sugars employed. The writer also has made a series of determinations with highly purified dextrose, lævulose, cane sugar and maltose; for all practical purposes the values referred to above may be taken as accurate.<sup>3</sup>

<sup>1</sup> *Trans.*, 1897, 71, 72.

<sup>2</sup> *Seventh Int. Congr. Appl. Chem.*, 1910, 1, 137.

<sup>3</sup> Compare Davis and Daish, *J. Agric., Sci.*, 1913, 5, 437.

Below are given the recent data obtained by Ling, Eynon and Lane.

Column (A) gives the weight of dry substance taken.

Column (B) gives the total weight of solution.

Column (C) gives the sp. gr. of the solution at 15.5°, referred to water at the same temperature.

Column (D) gives the grm. of sugar per 100 c.c. (reputed) (fluid grm. at 15.5°).

Column (E) gives the divisor for calculating grm. of sugar per 100 c.c. (reputed) from the sp. gr.

#### DEXTROSE.

A	B	C	D	E
0.9992	48.7130	1.007.97	2.0675	3.855
1.0034	48.1702	1.008.08	2.0999	3.848
1.9994	50.4500	1.015.45	4.0243	3.839
3.0003	51.4028	1.022.90	5.9705	3.836
4.0176	51.5618	1.030.72	8.0311	3.825
4.9977	51.8332	1.038.26	10.0108	3.822
5.9990	52.5148	1.045.61	11.9444	3.819
7.0012	52.6845	1.053.38	13.9984	3.813
7.9990	52.8802	1.061.13	16.0513	3.808
9.0015	53.3225	1.068.63	18.0398	3.804
9.9864	53.6794	1.076.03	20.0182	3.798
10.002	53.8410	1.084.06	22.1483	3.795
10.123	53.3030	1.092.42	24.4141	3.786

#### LÆVULOSE.

A	B	C	D	E
1.1040	51.2864	1.008.55	2.1710	3.938
2.0121	50.9296	1.015.76	4.0130	3.927
3.0125	51.3828	1.023.54	6.0008	3.923
4.0528	52.7696	1.031.05	7.9186	3.921
3.9982	51.5144	1.031.36	8.0047	3.918
5.0020	51.9567	1.039.18	10.0044	3.916
5.9136	52.7690	1.048.83	11.7202	3.910
6.9985	52.6476	1.054.73	14.0207	3.904
8.2876	54.7342	1.062.78	16.0922	3.901
8.9952	53.2702	1.070.43	18.0753	3.896
10.0312	54.0708	1.077.80	19.9949	3.890
11.0257	54.3534	1.085.57	22.0211	3.886
11.6614	52.9094	1.093.55	24.1021	3.881

#### MALTOSE.

A	B	C	D	E
0.9422	50.1806	1.007.46	1.8916	3.944
1.9977	50.9160	1.015.66	3.9250	3.930
3.1074	51.3990	1.024.31	6.1926	3.926
3.8939	51.4710	1.030.54	7.7963	3.917
5.0569	52.2945	1.039.34	10.0504	3.914
5.9907	53.6860	1.045.63	11.6680	3.911
7.0032	52.8330	1.054.63	13.9795	3.908
7.9710	53.4580	1.061.78	15.8319	3.902
8.0323	52.9998	1.062.87	16.1081	3.903
8.9098	53.2972	1.069.84	17.8847	3.905
8.9132	53.2600	1.069.91	17.9052	3.904
10.0734	53.7766	1.078.76	20.2073	3.898
10.9333	53.5393	1.086.47	22.1869	3.897
11.7828	54.2558	1.092.35	23.7227	3.893

For tables showing the sp. gr. of saccharose solutions at 20° compared with water at 4° as determined by the *Kaiserliche Normal Eichungskommission*, see *Zeit. Ver. Deutsch. Zuckerind.*, 1900, page 1123. These tables are given in full in Fröhling's *Anleitung für die Zuckerindustrie*, 7th Ed., 1911, pages 87-91.

**Refractometer Values.**—During the past few years the refractometer has found increasing application in sugar analysis and the opinion is growing that the refractometer is an indispensable instrument in all beet cultivation or sugar factory laboratories.<sup>1</sup> For recent tables of refractometric values see Main,<sup>2</sup> and Stanek.<sup>3</sup> Schönrock gives the following values which were determined in the laboratories of the Physikalische-technische Reichsanstalt, Berlin.

REFRACTIVE INDEX AND WATER CONTENT OF SUGAR SOLUTIONS.

$n_D^{20^\circ}$	w	$n_D^{20^\circ}$	w	$n_D^{20^\circ}$	w	$n_D^{20^\circ}$	w
1.3330	100	1.3590	83	1.3883	66	1.4221	49
1.3344	99	1.3606	82	1.3902	65	1.4242	48
1.3359	98	1.3622	81	1.3920	64	1.4264	47
1.3374	97	1.3639	80	1.3939	63	1.4285	46
1.3388	96	1.3655	79	1.3958	62	1.4307	45
1.3403	95	1.3672	78	1.3978	61	1.4329	44
1.3418	94	1.3689	77	1.3997	60	1.4351	43
1.3433	93	1.3706	76	1.4016	59	1.4373	42
1.3448	92	1.3723	75	1.4036	58	1.4396	41
1.3464	91	1.3740	74	1.4056	57	1.4418	40
1.3479	90	1.3758	73	1.4076	56	1.4441	39
1.3494	89	1.3775	72	1.4096	55	1.4464	38
1.3510	88	1.3793	71	1.4117	54	1.4486	37
1.3526	87	1.3811	70	1.4137	53	1.4509	36
1.3541	86	1.3829	69	1.4158	52	1.4532	35
1.3557	85	1.3847	68	1.4179	51	1.4555	34
1.3573	84	1.3865	67	1.4200	50		

**Relationship of Polarimetric Readings in Different Instruments.**—The following data for converting the readings obtained with different types of polarimeter are given by Brown, Morris and Millar.<sup>4</sup> The relationship of the readings obtained with a sodium light instrument to those obtained with a Ventzke-Scheibler instrument varies slightly according to the substance under observation and its concentration. The table given is therefore of considerable use in working with the different sugars.

Column A gives for each solution the result of dividing the scale reading of the Ventzke-Scheibler instrument by the circle reading of a Jellett-Cornu scale; it gives therefore the number of V.-S. scale divisions corresponding to 1° of the sodium-light scale. Column B gives the value of a scale division of the V.-S. instrument in terms of ray D.

Column C gives for each instrument the ratio of  $[\alpha]_j$  Biot to  $[\alpha]_D$ .

Column D gives the ratio of  $[\alpha]_j$ , Montgolfier to  $[\alpha]_D$ . For a discussion of

<sup>1</sup> Compare Pellet, *Int. Sugar J.*, 1914, 16, 521.

<sup>2</sup> *Int. Sugar J.*, 9, 481.

<sup>3</sup> *Zeit. Ver. Deutsch. Zuckerind.*, 61, 421.

<sup>4</sup> *Trans.*, 1897, 71, 93.



the relationship existing in each case between  $[\alpha]_D$  Biot (Biot's *jaune moyen*) and  $[\alpha]_D$  Montgolfier see Brown, Morris and Millar (*loc. cit.*).

	Concentration.	A	B	C	D
Saccharose.....	10 %	2.882	0.3469	1.107	1.130
Maltose.....	10 %	2.899	0.3449	1.113	1.136
Maltose.....	5 %	2.892	0.3457	1.111	1.134
Dextrose.....	10 %	2.904	0.3442	1.115	1.138
Dextrose.....	5 %	2.894	0.3454	1.111	1.134
Starch products.....	10 %	2.891	0.3458	1.111	1.134
Starch products.....	5 %	2.895	0.3454	1.111	1.134

**General Methods.**—Certain sources of error in estimating sugars by gravimetric and volumetric methods are dealt with in a paper by Davis and Daish.<sup>1</sup> In the gravimetric method, in which the precipitate of cuprous oxide obtained is collected on asbestos, the necessity of previously digesting the asbestos with boiling 20% sodium hydroxide solution and subsequently thoroughly washing with water is emphasised; unless the asbestos is treated in this way considerable loss of weight may occur owing to the action of the hot Fehling solution on impurities present in the asbestos. It is probably best and simplest to collect the cuprous oxide precipitate in a Gooch crucible containing a layer  $\frac{1}{4}$  to  $\frac{1}{2}$  in. thick of the purified asbestos and, after thoroughly washing with boiling water, to wash with a little alcohol and ether and dry in a steam oven. The Gooch crucible is then placed in an ordinary No. 1 Berlin crucible (which serves to shield it from direct contact with the flame) and is heated strongly over a  $\frac{1}{2}$ -in. Teclu or Fletcher Argand gas flame for  $\frac{1}{2}$  hour; it is then allowed to cool in the desiccator at least 1 hour, weighed and again heated for another 30 minutes. The weight is generally practically constant after the first heating, the increase of weight in the second heating seldom exceeding 0.0005 grm. If the Gooch crucible is shielded from direct contact with the flame in the way indicated there is never any difficulty in obtaining accurate results for the weight of cupric oxide and the process is far more simple and rapid than collecting the cuprous oxide in a Soxhlet tube and reducing to copper in a stream of hydrogen in the manner generally advocated. The same crucible and asbestos can be used over and over again for 10 to 20 successive charges without dissolving away the cupric oxide; the fresh charge of cuprous oxide is collected on the top of the previous charge of cupric oxide. It is only necessary to ensure that this is constant in weight. Elion<sup>2</sup> and others have stated that conversion to cupric oxide gives unreliable and discordant results, but this is not true when the cupric oxide is shielded from the reducing gases of the flame. Under the conditions given the ratio of  $\frac{2\text{CuO}}{\text{Cu}_2\text{O}}$  is found to be 1.111 to 1.112 the theoretical ratio (Cu = 63.57) being 1.112. H. Pellet (*Private*

<sup>1</sup> *J. Agric. Science*, 1913, 5, 437.

<sup>2</sup> *Zell. angew. Chem.*, 1890, 325.

*Communication*) recommends igniting the cuprous oxide precipitate by heating it *at not too high a temperature* in a muffle furnace. A blowpipe should never be used, even when the Gooch crucible is shielded by an outer crucible, as low results are then obtained, probably owing to the slight dissociation of cupric oxide which occurs at very high temperatures: the ratio  $\frac{2\text{CuO}}{\text{Cu}_2\text{O}}$  when the blowpipe is used ranges from 1.105 to 1.109 instead of having practically the theoretical value 1.112 (Davis and Daish, *loc. cit.*).

The recommendation is frequently made to weigh the cuprous oxide, as such, after drying at 100° and this method has been prescribed by the U. S. Bureau of Chemistry<sup>1</sup> as one of its provisional methods. Whilst this course is quite safe in the case of pure sugars it involves considerable error when dealing with impure solutions containing organic substances such as are obtained when working with plant or animal extracts, even when these have been partially purified by treatment with basic lead acetate, etc.; the same is true of the solutions obtained on inverting or hydrolysing starch or sugars by enzyme preparations, such as diastase, maltase or invertase, or after fermenting sugars by yeasts, even though alumina cream is subsequently used to clear the solutions. In all such cases, the cuprous oxide invariably contains organic matter, which burns away during ignition, so that the ratio  $\frac{\text{CuO}}{\text{Cu}_2\text{O}}$  is thereby diminished; this ratio varies from 1.060 to 1.105, according to the nature of the solution and of the enzyme preparation employed. It is probable that in dealing with yeasts, invertase, etc., the cuprous oxide precipitate contains traces of copper compounds of amino-acids, proteins, etc., as well as colloidal matter carried down by adsorption. In such cases the cupric oxide weighed would be slightly higher than that actually due to reduction only; but numerous experiments indicate that this error is relatively small and not likely to interfere with the results obtained. An alternative method of procedure in such cases is to estimate the actual copper present in the cuprous oxide precipitate by one of the standard volumetric methods; the A. O. A. C. have recently adopted as a provisional process Low's thiosulphate method (see below, page 41). H. Pellet<sup>2</sup> advocates the use of potassium cyanide (Parker's method) under the conditions worked out by C. Müller.<sup>3</sup>

The method which depends on using ferric sulphate to dissolve the cuprous oxide and subsequently titrating back with permanganate, is criticised by Davis and Daish (*loc. cit.*) who came to the conclusion that it cannot be regarded as one of the most accurate methods for the purpose. This method has, however, been widely used in recent years and has been adopted as provisional by the A. O. A. C.<sup>4</sup> In biochemical work it has been extensively

<sup>1</sup> *Bulletin* 107 (revised), 1912, page 53. Allen Vol. I, page 325.

<sup>2</sup> *Bull. Assoc. Chem. Sacr.*, 1914, 915.

<sup>3</sup> *Bull. Assoc. Chem. Sacr.*, 1911-1912, page 71.

<sup>4</sup> *Bulletin* 107 (revised), 1912, page 52. Allen, Vol. I, page 324.

employed since Bertrand advocated its use<sup>1</sup> and gave tables for dextrose, invert sugar, maltose and lactose. Davis and Daish state that in their hands this method gave values from 1 to 1.5% in error for pure dextrose and maltose and point out that the constants given by Bertrand for his dextrose ( $[\alpha]_D = 52.0^\circ$ ) and maltose ( $137.4^\circ$ ) are not those of sugars of the highest degree of purity. In preparing the solution of invert sugar on which his tables are based, Bertrand hydrolysed cane sugar by heating with 2% hydrochloric acid for 10 to 15 minutes at  $100^\circ$ ; such treatment invariably causes slight destruction of l  vulose and Davis and Daish in consequence found results by using Bertrand's tables which were 3 to 5% low. That decomposition of invert sugar occurs with dilute hydrochloric acid at temperatures above  $70^\circ$  has been generally recognised since the work of Herzfeld.<sup>2</sup> The volumetric method using permanganate is, too, not so advantageous as the method of Ling, Rendle and Jones (see below, page 38) either on the ground of rapidity (for which it is generally preferred to gravimetric methods) or of accuracy. It is to be regarded only as a fairly rapid approximate method which may prove useful when no high degree of accuracy is required.

**Gravimetric Methods for Reducing Sugars.**—Probably the most accurate method of estimating the reducing sugars (dextrose, l  vulose, invert sugar and maltose) is to work under the conditions laid down by Brown, Morris and Millar<sup>3</sup> employing the tables they have given for these sugars. Davis and Daish using highly purified specimens of the sugars verified these tables and found a quite satisfactory agreement. The probable error in the copper oxide weighed under these conditions is not likely to be more than 1 mg., which, when 0.20 to 0.40 grm. is actually obtained, gives an error well within 0.5%. It is certainly preferable in the majority of cases to work under the well-defined conditions laid down by Brown, Morris and Millar than to use Allihn's method, in which the size of the beaker, the kind and height of the flame, undoubtedly influence the results; the shortness of the time of heating is, too, a disadvantage, as any slight differences thus exercise proportionately greater effect. The tables given by Wein for maltose, which have been very generally used (see Allen, Vol. I, page 363) and have been provisionally adopted in the United States (*Bulletin* 107 *revised*) were shown by Brown, Morris and Millar in 1897 to give results 5% low; Ling and Baker<sup>4</sup> confirmed this.

**Brown, Morris and Millar's Method.**—This is a modification of the gravimetric process suggested by O'Sullivan<sup>5</sup> the essential point being that regular heating is ensured by immersing the beaker during the reduction in boiling water; the time of heating is 12 minutes. The solutions used are as follows:

<sup>1</sup> *Bull. Soc. Chim.*, 1906 [iii], 35, 1285.

<sup>2</sup> *Zeit. Ver. Zuck. Ind.*, 1898, 699 and 742.

<sup>3</sup> *Trans.*, 1897, 71, 105.

<sup>4</sup> *Trans.*, 1897, 71, 509.

<sup>5</sup> *Trans.*, 1876, 30, 150.

A. Recrystallised copper sulphate	34.6 gm.
Water to	500 c.c.
B. Rochelle salt	173.0 gm.
Anhydrous sodium hydroxide	65.0 gm.
Water to	500 c.c.

As the oxidising power of the solution is very sensitive to small changes in the amount of alkali present great care must be taken to ensure accuracy in the weight of sodium hydroxide. This is best done by preparing a somewhat concentrated solution of sodium hydroxide (free from carbonate), ascertaining the strength by means of the density, and then diluting so that a known volume (300 c.c. for example) represents exactly 65.0 gm. It is convenient to prepare large volumes (7 to 10 litres) of each of the solutions A and B and to store these in large glass bottles (Welsbach bottles) so arranged as to feed two 25 c.c. automatic pipettes. Access of carbon dioxide of the air to solution B should be guarded against by a U-tube containing soda-lime.

25 c.c. of each solution A and B are introduced into a beaker, the surface area of which<sup>1</sup> is 44 sq. cm.; the beaker is covered with a clock glass and immersed in a bath of *boiling* water until the temperature of the solution is the same as that of the bath. This is usually the case in 6 minutes. The sugar solution is now added and the total volume diluted if necessary to 100 c.c.; it is best if possible to have the sugar solution of such a concentration that 50 c.c. can be taken directly for the estimation. If the sugar solution is considerably more concentrated, 25 c.c. (or 30 c.c.) are taken and a corresponding quantity of boiling water (25 c.c. or 20 c.c.) added. The beaker is then immediately covered with the clock glass and heated exactly 12 minutes in boiling water; the precipitated cuprous oxide is then filtered as rapidly as possible through a Soxhlet tube or preferably a Gooch crucible, thoroughly washed with about 400 c.c. of boiling water, dried and weighed, either as cupric oxide (ignition as above) or after reduction to metallic copper.

The amount of reducing sugar taken for an estimation should give a weight of cupric oxide lying within the limits 0.15 to 0.40 gm. Tables I and II give the relationship existing between the weight of copper (or of CuO) and the various sugars.

A convenient heating bath is shown in Fig. 1 for use with the beaker flasks employed in the reduction (Davis and Daish, *loc. cit.*). It consists of a 10-in. enamelled iron saucepan, 4½ in. deep, into which a false bottom of copper plate is placed so as to afford a convenient support for the beaker flasks. The cover of the bath is made of copper and consists of two halves each perforated with two 2½-in. holes, the edge of the plate being

<sup>1</sup> A Jena beaker flask of 250 c.c. can be conveniently used here; such vessels, with a top diameter 2¼ in., bottom diameter 2⅞ in., give accurately the results contained in Brown, Morris and Millar's tables (Davis and Daish, *loc. cit.*), and are far more convenient in manipulation than ordinary beakers. Pellet also (*Bull. Assoc. Chem. Sucr.*, 1913, 198) has independently suggested the use of beaker flasks for measurements of the reducing power of sugars.

turned down so as to fit over the bath. Each half of the cover can be lifted off separately so as to admit the beaker flask containing the Fehling solution; with this arrangement several beaker-flasks can be heated simultaneously.

The most carefully prepared Fehling solution usually gives a very slight precipitate of cuprous oxide on heating, owing to spontaneous reduction; this value should be determined for every fresh batch of solution and be allowed for in the final result of each determination. It usually amounts to

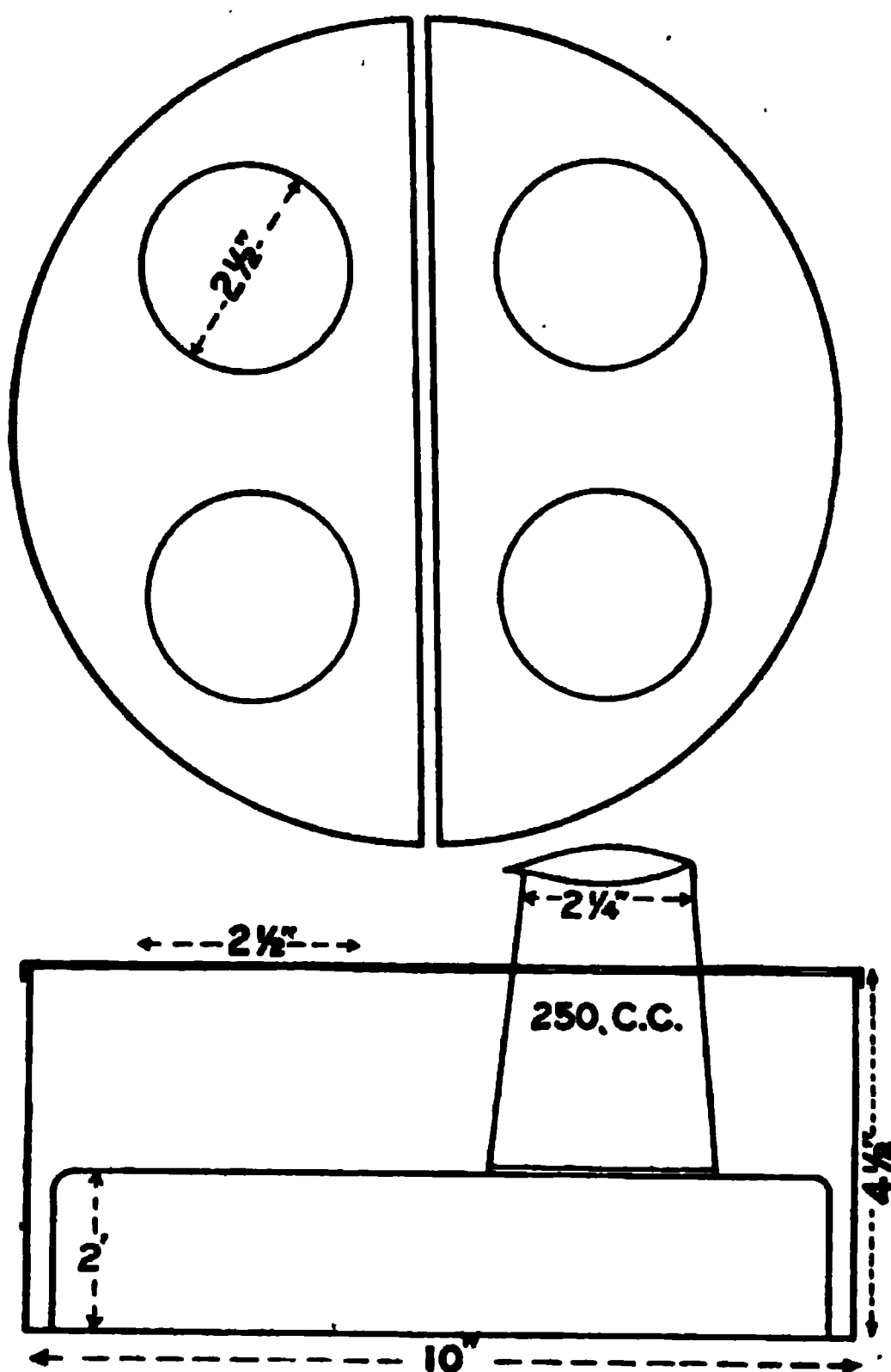


Fig. 1.

0.002 to 0.003 gram. per 50 c.c. of Fehling solution. The writer finds that when the two solutions A and B after being prepared are separately stored in stoppered bottles for a week or fortnight before use a considerable quantity of sediment separates from each; when the solutions are filtered and then tested in the usual way, in a "blank" experiment, the amount of self-reduction is very small, usually 0.0000 to 0.0010 gram. per 50 c.c. of solution. The "self-reduction" thus rapidly diminishes immediately after the solutions are made up, so that it is always advisable to store the solutions for at least a fortnight before use.

TABLE I.—REDUCING POWER OF DEXTROSE, LÆVULOSE AND INVERT SUGAR UNDER BROWN, MORRIS AND MILLAR'S CONDITIONS.

Sugar, mg.	Dextrose			Lævulose			Invert sugar		
	Cu, grm.	CuO, grm.	CuO corre- sponding to 1 grm.	Cu, grm.	CuO, grm.	CuO corre- sponding to 1 grm.	Cu, grm.	CuO, grm.	CuO corre- sponding to 1 grm.
50	0.1030	0.1289	2.578	0.0923	0.1155	2.340	0.0975	0.1221	2.442
55	0.1134	0.1422	2.585	0.1027	0.1287	2.341	0.1076	0.1349	2.453
60	0.1238	0.1552	2.587	0.1122	0.1407	2.345	0.1176	0.1474	2.457
65	0.1342	0.1682	2.589	0.1216	0.1524	2.346	0.1275	0.1598	2.459
70	0.1443	0.1809	2.585	0.1312	0.1645	2.350	0.1373	0.1721	2.459
75	0.1543	0.1935	2.580	0.1405	0.1761	2.349	0.1468	0.1840	2.454
80	0.1644	0.2061	2.577	0.1500	0.1881	2.351	0.1566	0.1963	2.454
85	0.1740	0.2187	2.572	0.1590	0.1993	2.345	0.1662	0.2084	2.451
90	0.1834	0.2299	2.555	0.1686	0.2114	2.349	0.1755	0.2200	2.445
95	0.1930	0.2420	2.547	0.1774	0.2224	2.341	0.1848	0.2317	2.439
100	0.2027	0.2538	2.538	0.1862	0.2331	2.331	0.1941	0.2430	2.430
105	0.2123	0.2662	2.535	0.1952	0.2447	2.331	0.2034	0.2550	2.429
110	0.2218	0.2781	2.528	0.2040	0.2558	2.325	0.2128	0.2668	2.425
115	0.2313	0.2900	2.522	0.2129	0.2669	2.321	0.2220	0.2783	2.420
120	0.2404	0.3014	2.512	0.2215	0.2777	2.314	0.2311	0.2898	2.415
125	0.2496	0.3130	2.504	0.2303	0.2887	2.310	0.2400	0.3009	2.407
130	0.2585	0.3241	2.493	0.2390	0.2997	2.305	0.2489	0.3121	2.400
135	0.2675	0.3354	2.484	0.2477	0.3106	2.300	0.2578	0.3232	2.394
140	0.2762	0.3463	2.473	0.2559	0.3209	2.292	0.2663	0.3339	2.385
145	0.2850	0.3573	2.464	0.2641	0.3311	2.284	0.2750	0.3448	2.378
150	0.2934	0.3673	2.448	0.2723	0.3409	2.273	0.2832	0.3546	2.364
155	0.3020	0.3787	2.443	0.2805	0.3517	2.269	0.2915	0.3655	2.358
160	0.3103	0.3891	2.432	0.2889	0.3622	2.264	0.3002	0.3764	2.352
165	0.3187	0.3996	2.422	0.2972	0.3726	2.258	0.3086	0.3869	2.345
170	0.3268	0.4098	2.410	0.3053	0.3828	2.252	0.3167	0.3971	2.336
175	0.3350	0.4200	2.400	0.3134	0.3930	2.245	0.3251	0.4076	2.329
180	0.3431	0.4302	2.390	0.3216	0.4032	2.240	0.3331	0.4177	2.320
185	0.3508	0.4399	2.377	0.3297	0.4134	2.234	0.3410	0.4276	2.311
190	0.3590	0.4501	2.369	0.3377	0.4234	2.228	0.3490	0.4376	2.303
195	0.3668	0.4599	2.358	0.3457	0.4335	2.223	0.3570	0.4476	2.295
200	0.3745	0.4689	2.344	0.3539	0.4431	2.216	0.3650	0.4570	2.285
205	0.3822	0.4792	2.338	0.3616	0.4534	2.211	0.3726	0.4672	2.279

TABLE II.—REDUCING POWER OF MALTOSE UNDER BROWN, MORRIS AND MILLAR'S CONDITIONS.

Maltose, mg.	Cu weighed, grm.	CuO weighed, grm.	CuO corre- sponding to 1 grm. maltose	Maltose, mg.	Cu weighed, grm.	CuO weighed, grm.	CuO corre- sponding to 1 grm. maltose
70	0.0772	0.0966	1.380	190	0.2072	0.2593	1.371
75	0.0826	0.1034	1.380	195	0.2126	0.2661	1.370
80	0.0880	0.1102	1.379	200	0.2180	0.2729	1.370
85	0.0934	0.1169	1.379	205	0.2234	0.2797	1.370
90	0.0988	0.1237	1.378	210	0.2288	0.2865	1.369
95	0.1042	0.1305	1.378	215	0.2342	0.2933	1.369
100	0.1097	0.1373	1.378	220	0.2397	0.3000	1.3685
105	0.1151	0.1441	1.377	225	0.2451	0.3068	1.368
110	0.1205	0.1509	1.377	230	0.2505	0.3136	1.368
115	0.1259	0.1576	1.3765	235	0.2559	0.3203	1.367
120	0.1313	0.1644	1.376	240	0.2613	0.3272	1.367
125	0.1367	0.1712	1.376	245	0.2667	0.3340	1.3665
130	0.1422	0.1779	1.375	250	0.2722	0.3407	1.366
135	0.1476	0.1848	1.375	255	0.2776	0.3475	1.366
140	0.1530	0.1916	1.375	260	0.2830	0.3543	1.365
145	0.1584	0.1983	1.374	265	0.2884	0.3610	1.365
150	0.1634	0.2051	1.374	270	0.2938	0.3678	1.365
155	0.1692	0.2119	1.373	275	0.2992	0.3747	1.364
160	0.1747	0.2186	1.373	280	0.3047	0.3814	1.364
165	0.1801	0.2254	1.373	285	0.3101	0.3882	1.3635
170	0.1855	0.2323	1.372	290	0.3155	0.3950	1.363
175	0.1909	0.2390	1.372	295	0.3209	0.4017	1.363
180	0.1963	0.2458	1.3715	300	0.3264	0.4085	1.362
185	0.2017	0.2526	1.371	305	0.3318	0.4154	1.362



## PROVISIONAL UNITED STATES A. O. A. C. GRAVIMETRIC METHOD FOR REDUCING SUGARS.

The following are the conditions which have been adopted as provisional by the A. O. A. C.,<sup>1</sup> the tables are due to Munson and Walker.<sup>2</sup>

### (1) Preparation of Solutions and Asbestos.

(a) **Solutions.**—Use the solutions in Vol. I, page 318, under Soxhlet's modification of Fehling's solution.<sup>3</sup>

(b) **Asbestos.**—Prepare the asbestos, which should be the amphibole variety, by first digesting with 1:3 hydrochloric acid for 2 or 3 days. Wash free from acid and digest for a similar period with sodium hydroxide solution, after which treat for a few hours with hot alkaline copper tartrate solution of the strength employed in sugar determinations. Then wash the asbestos free from alkali, finally digest with nitric acid for several hours and after washing free from acid shake with water for use. In preparing the Gooch crucible load it with a film of asbestos  $\frac{1}{4}$  in. thick, wash this thoroughly with water to remove fine particles of asbestos; finally wash with alcohol and ether, dry for 30 minutes at 100° C., cool in a desiccator and weigh. It is best to dissolve the cuprous oxide with nitric acid each time after weighing and use the same felts over and over again, as they improve with use.

### (2) Determination.

Transfer 25 c.c. each of the copper and alkaline tartrate solutions to a 400 c.c. Jena or Non-sol beaker and add 50 c.c. of reducing sugar solution, or, if a smaller volume of sugar solution be used, add water to make the final volume 100 c.c. Heat the beaker upon an asbestos gauze over a Bunsen burner, so regulate the flame that boiling begins in 4 minutes, and continue the boiling for exactly 2 minutes. Keep the beaker covered with a watch-glass throughout the entire time of heating. Without diluting, filter the cuprous oxide at once on an asbestos felt in a porcelain Gooch crucible, using suction. Wash the cuprous oxide thoroughly with water at a temperature of about 60° C., then with 10 c.c. of alcohol and finally with 10 c.c. of ether. Dry for 30 minutes in a water oven at 100° C., cool in a desiccator and *weigh as cuprous oxide*.

N. B. The number of milligrams of copper reduced by a given amount of reducing sugar differs when saccharose is present and when it is absent. In the tables following, the absence of saccharose is assumed except in the two columns under invert sugar, where one for mixtures of invert sugar and saccharose (0.4 gram. of total sugar in 50 c.c. of solution) and one for invert sugar and saccharose when the 50 c.c. of solution contains 2 gram. of total sugar are given, in addition to the column for invert sugar alone.

<sup>1</sup> *Bulletin* 107 (revised), 1912, page 241.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1906, 28, 663; 1907, 29, 541.

<sup>3</sup> The tartrate solution used by the A. O. A. C. contains 173 gram. of Rochelle salt, and 50 gram. of sodium hydroxide in 500 c.c.

TABLE FOR CALCULATING DEXTROSE, INVERT SUGAR ALONE, INVERT SUGAR IN THE PRESENCE OF SACCHAROSE (0.4 GRM. AND 2 GRM. TOTAL SUGAR), LACTOSE (THREE FORMS), AND MALTOSE (ANHYDROUS AND CRYSTALLISED).

(For Lactose Figures see pages 58 to 61.)

(Expressed in milligrams.)

Cuprous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Dextrose (d-glucose)	Invert sugar	Invert sugar and saccharose		Maltose		Cuprous oxide (Cu <sub>2</sub> O)
				0.4 gm. total sugar	2 gm. total sugar	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	$\frac{1}{2}$ C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> + H <sub>2</sub> O.	
10	8.9	4.0	4.5	1.6	.....	5.9	6.8	10
11	9.8	4.5	5.0	2.1	.....	6.7	7.0	11
12	10.7	4.9	5.4	2.5	.....	7.5	7.9	12
13	11.5	5.3	5.8	3.0	.....	8.3	8.7	13
14	12.4	5.7	6.3	3.4	.....	9.1	9.5	14
15	13.3	6.2	6.7	3.9	.....	9.9	10.4	15
16	14.2	6.6	7.2	4.3	.....	10.6	11.2	16
17	15.1	7.0	7.6	4.8	.....	11.4	12.0	17
18	16.0	7.5	8.1	5.2	.....	12.2	12.9	18
19	16.9	7.9	8.5	5.7	.....	13.0	13.7	19
20	17.8	8.3	8.9	6.1	.....	13.8	14.6	20
21	18.7	8.7	9.4	6.6	.....	14.6	15.4	21
22	19.5	9.2	9.8	7.0	.....	15.4	16.2	22
23	20.4	9.6	10.3	7.5	.....	16.2	17.1	23
24	21.3	10.0	10.7	7.9	.....	17.0	17.9	24
25	22.2	10.5	11.2	8.4	.....	17.8	18.7	25
26	23.1	10.9	11.6	8.8	.....	18.6	19.6	26
27	24.0	11.3	12.0	9.3	.....	19.4	20.4	27
28	24.9	11.8	12.5	9.7	.....	20.2	21.2	28
29	25.8	12.2	12.9	10.2	.....	21.0	22.1	29
30	26.6	12.6	13.4	10.7	4.3	21.8	22.9	30
31	27.5	13.1	13.8	11.1	4.7	22.6	23.7	31
32	28.4	13.5	14.3	11.6	5.2	23.3	24.6	32
33	29.3	13.9	14.7	12.0	5.6	24.1	25.4	33
34	30.2	14.3	15.2	12.5	6.1	24.9	26.2	34
35	31.1	14.8	15.6	12.9	6.5	25.7	27.1	35
36	32.0	15.2	16.1	13.4	7.0	26.5	27.9	36
37	32.9	15.6	16.5	13.8	7.4	27.3	28.7	37
38	33.8	16.1	16.9	14.3	7.9	28.1	29.6	38
39	34.6	16.5	17.4	14.7	8.4	28.9	30.4	39
40	35.5	16.9	17.8	15.2	8.8	29.7	31.3	40
41	36.4	17.4	18.3	15.6	9.3	30.5	32.1	41
42	37.3	17.8	18.7	16.1	9.7	31.3	32.9	42
43	38.2	18.2	19.2	16.6	10.2	32.1	33.8	43
44	39.1	18.7	19.6	17.0	10.7	32.9	34.6	44
45	40.0	19.1	20.1	17.5	11.1	33.7	35.4	45
46	40.9	19.6	20.5	17.9	11.6	34.4	36.3	46
47	41.7	20.0	21.0	18.4	12.0	35.2	37.1	47
48	42.6	20.4	21.4	18.8	12.5	36.0	37.9	48
49	43.5	20.9	21.9	19.3	12.9	36.8	38.8	49
50	44.4	21.3	22.3	19.7	13.4	37.6	39.6	50
51	45.3	21.7	22.8	20.2	13.9	38.4	40.4	51
52	46.2	22.2	23.2	20.7	14.3	39.2	41.3	52
53	47.1	22.6	23.7	21.1	14.8	40.0	42.1	53
54	48.0	23.0	24.1	21.6	15.2	40.8	42.9	54
55	48.9	23.5	24.6	22.0	15.7	41.6	43.8	55
56	49.7	23.9	25.0	22.5	16.2	42.4	44.6	56
57	50.6	24.3	25.5	22.9	16.6	43.2	45.4	57
58	51.5	24.8	25.9	23.4	17.1	44.0	46.3	58
59	52.4	25.2	26.4	23.9	17.5	44.8	47.1	59
60	53.3	25.6	26.8	24.3	18.0	45.6	48.0	60
61	54.2	26.1	27.3	24.8	18.5	46.3	48.8	61
62	55.1	26.5	27.7	25.2	18.9	47.1	49.6	62
63	56.0	27.0	28.2	25.7	19.4	47.9	50.5	63
64	56.8	27.4	28.6	26.2	19.8	48.7	51.3	64



TABLE FOR CALCULATING DEXTROSE, INVERT SUGAR ALONE, INVERT SUGAR IN THE PRESENCE OF SACCHAROSE (0.4 GRM. AND 2 GRM. TOTAL SUGAR), LACTOSE (THREE FORMS), AND MALTOSE (ANHYDROUS AND CRYSTALLISED).

(For Lactose Figures see pages 58 to 61.)—Continued.

(Expressed in milligrams.)

Cuprous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Dextrose (d-glu- cose)	Invert sugar	Invert sugar and saccharose		Maltose		Cuprous oxide (Cu <sub>2</sub> O)
				0.4 grm. total sugar	2 grm. total sugar	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> + H <sub>2</sub> O	
65	57.7	27.8	29.1	26.6	20.3	49.5	52.1	65
66	58.6	28.3	29.5	27.1	20.8	50.3	53.0	66
67	59.5	28.7	30.0	27.5	21.2	51.1	53.8	67
68	60.4	29.2	30.4	28.0	21.7	51.9	54.6	68
69	61.3	29.6	30.9	28.5	22.2	52.7	55.5	69
70	62.2	30.0	31.3	28.9	22.6	53.5	56.3	70
71	63.1	30.5	31.8	29.4	23.1	54.3	57.1	71
72	64.0	30.9	32.3	29.8	23.5	55.1	58.0	72
73	64.8	31.4	32.7	30.3	24.0	55.9	58.8	73
74	65.7	31.8	33.2	30.8	24.5	56.7	59.6	74
75	66.6	32.2	33.6	31.2	24.9	57.5	60.5	75
76	67.5	32.7	34.1	31.7	25.4	58.2	61.3	76
77	68.4	33.1	34.5	32.1	25.9	59.0	62.1	77
78	69.3	33.6	35.0	32.6	26.3	59.8	63.0	78
79	70.2	34.0	35.4	33.1	26.8	60.6	63.8	79
80	71.1	34.4	35.9	33.5	27.3	61.4	64.6	80
81	71.9	34.9	36.3	34.0	27.7	62.2	65.5	81
82	72.8	35.3	36.8	34.5	28.2	63.0	66.3	82
83	73.7	35.8	37.3	34.9	28.6	63.8	67.1	83
84	74.6	36.2	37.7	35.4	29.1	64.6	68.0	84
85	75.5	36.7	38.2	35.8	29.6	65.4	68.8	85
86	76.4	37.1	38.6	36.3	30.0	66.2	69.7	86
87	77.3	37.5	39.1	36.8	30.5	67.0	70.5	87
88	78.2	38.0	39.5	37.2	31.0	67.8	71.3	88
89	79.1	38.4	40.0	37.7	31.4	68.5	72.2	89
90	79.9	38.9	40.4	38.2	31.9	69.3	73.0	90
91	80.8	39.3	40.9	38.6	32.4	70.1	73.8	91
92	81.7	39.8	41.4	39.1	32.8	70.9	74.7	92
93	82.6	40.2	41.8	39.6	33.3	71.7	75.5	93
94	83.5	40.6	42.3	40.0	33.8	72.5	76.3	94
95	84.4	41.1	42.7	40.5	34.2	73.3	77.2	95
96	85.3	41.5	43.2	41.0	34.7	74.1	78.0	96
97	86.2	42.0	43.7	41.4	35.2	74.9	78.8	97
98	87.1	42.4	44.1	41.9	35.6	75.7	79.7	98
99	87.9	42.9	44.6	42.4	36.1	76.5	80.5	99
100	88.8	43.3	45.0	42.8	36.6	77.3	81.3	100
101	89.7	43.8	45.5	43.3	37.0	78.1	82.2	101
102	90.6	44.2	46.0	43.8	37.5	78.8	83.0	102
103	91.5	44.7	46.4	44.2	38.0	79.6	83.8	103
104	92.4	45.1	46.9	44.7	38.5	80.4	84.7	104
105	93.3	45.5	47.3	45.2	38.9	81.2	85.5	105
106	94.2	46.0	47.8	45.6	39.4	82.0	86.3	106
107	95.0	46.4	48.3	46.1	39.9	82.8	87.2	107
108	95.9	46.9	48.7	46.6	40.3	83.6	88.0	108
109	96.8	47.3	49.2	47.0	40.8	84.4	88.8	109
110	97.7	47.8	49.6	47.5	41.3	85.2	89.7	110
111	98.6	48.2	50.1	48.0	41.7	86.0	90.5	111
112	99.5	48.7	50.6	48.4	42.2	86.8	91.3	112
113	100.4	49.1	51.0	48.9	42.7	87.6	92.2	113
114	101.3	49.6	51.5	49.4	43.2	88.4	93.0	114
115	102.2	50.0	51.9	49.8	43.6	89.2	93.9	115
116	103.0	50.5	52.4	50.3	44.1	90.0	94.7	116
117	103.9	50.9	52.9	50.8	44.6	90.7	95.5	117
118	104.8	51.4	53.3	51.2	45.0	91.5	96.4	118
119	105.7	51.8	53.8	51.7	45.5	92.3	97.2	119

TABLE FOR CALCULATING DEXTROSE, INVERT SUGAR ALONE, INVERT SUGAR IN THE PRESENCE OF SACCHAROSE (0.4 GRM. AND 2 GRM. TOTAL SUGAR), LACTOSE (THREE FORMS), AND MALTOSE (ANHYDROUS AND CRYSTALLISED).

(For Lactose Figures see pages 58 to 61.)—Continued.  
(Expressed in milligrams.)

Cuprous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Dextrose (d-glu- cose)	Invert sugar	Invert sugar and saccharose		Maltose		Cuprous oxide (Cu <sub>2</sub> O)
				0.4 grm. total sugar	2 grm. total sugar	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> + H <sub>2</sub> O	
120	106.6	52.3	54.3	52.2	46.0	93.1	98.0	120
121	107.5	52.7	54.7	52.7	46.5	93.9	98.9	121
122	108.4	53.2	55.2	53.1	46.9	94.7	99.7	122
123	109.3	53.6	55.7	53.6	47.4	95.5	100.5	123
124	110.1	54.1	56.1	54.1	47.9	96.3	101.4	124
125	111.0	54.5	56.6	54.5	48.3	97.1	102.2	125
126	111.9	55.0	57.0	55.0	48.8	97.9	103.0	126
127	112.8	55.4	57.5	55.5	49.3	98.7	103.9	127
128	113.7	55.9	58.0	55.9	49.8	99.4	104.7	128
129	114.6	56.3	58.4	56.4	50.2	100.2	105.5	129
130	115.5	56.8	58.9	56.9	50.7	101.0	106.4	130
131	116.4	57.2	59.4	57.4	51.2	101.8	107.2	131
132	117.3	57.7	59.8	57.8	51.7	102.6	108.0	132
133	118.1	58.1	60.3	58.3	52.1	103.4	108.9	133
134	119.0	58.6	60.8	58.8	52.6	104.2	109.7	134
135	119.9	59.0	61.2	59.3	53.1	105.0	110.5	135
136	120.8	59.5	61.7	59.7	53.6	105.8	111.4	136
137	121.7	60.0	62.2	60.2	54.0	106.6	112.2	137
138	122.6	60.4	62.6	60.7	54.5	107.4	113.0	138
139	123.5	60.9	63.1	61.2	55.0	108.2	113.9	139
140	124.4	61.3	63.6	61.6	55.5	109.0	114.7	140
141	125.2	61.8	64.0	62.1	55.9	109.8	115.5	141
142	126.1	62.2	64.5	62.6	56.4	110.5	116.4	142
143	127.0	62.7	65.0	63.1	56.9	111.3	117.2	143
144	127.9	63.1	65.4	63.5	57.4	112.1	118.0	144
145	128.8	63.6	65.9	64.0	57.8	112.9	118.9	145
146	129.7	64.0	66.4	64.5	58.3	113.7	119.7	146
147	130.6	64.5	66.9	65.0	58.8	114.5	120.5	147
148	131.5	65.0	67.3	65.4	59.3	115.3	121.4	148
149	132.4	65.4	67.8	65.9	59.7	116.1	122.2	149
150	133.2	65.9	68.3	66.4	60.2	116.9	123.0	150
151	134.1	66.3	68.7	66.9	60.7	117.7	123.9	151
152	135.0	66.8	69.2	67.3	61.2	118.5	124.7	152
153	135.9	67.2	69.7	67.8	61.7	119.3	125.5	153
154	136.8	67.7	70.1	68.3	62.1	120.0	126.4	154
155	137.7	68.2	70.6	68.8	62.6	120.8	127.2	155
156	138.6	68.6	71.1	69.2	63.1	121.6	128.0	156
157	139.5	69.1	71.6	69.7	63.6	122.4	128.9	157
158	140.3	69.5	72.0	70.2	64.1	123.2	129.7	158
159	141.2	70.0	72.5	70.7	64.5	124.0	130.5	159
160	142.1	70.4	73.0	71.2	65.0	124.8	131.4	160
161	143.0	70.9	73.4	71.6	65.5	125.6	132.2	161
162	143.9	71.4	73.9	72.1	66.0	126.4	133.0	162
163	144.8	71.8	74.4	72.6	66.5	127.2	133.9	163
164	145.7	72.3	74.9	73.1	66.9	128.0	134.7	164
165	146.6	72.8	75.3	73.6	67.4	128.8	135.5	165
166	147.5	73.2	75.8	74.0	67.9	129.6	136.4	166
167	148.3	73.7	76.3	74.5	68.4	130.3	137.2	167
168	149.2	74.1	76.8	75.0	68.9	131.1	138.0	168
169	150.1	74.6	77.2	75.5	69.3	131.9	138.9	169
170	151.0	75.1	77.7	76.0	69.8	132.7	139.7	170
171	151.9	75.5	78.2	76.4	70.3	133.5	140.5	171
172	152.8	76.0	78.7	76.9	70.8	134.3	141.4	172
173	153.7	76.4	79.1	77.4	71.3	135.1	142.2	173
174	154.6	76.9	79.6	77.9	71.7	135.9	143.0	174

TABLE FOR CALCULATING DEXTROSE, INVERT SUGAR ALONE, INVERT SUGAR IN THE PRESENCE OF SACCHAROSE (0.4 GRM. AND 2 GRM. TOTAL SUGAR), LACTOSE (THREE FORMS), AND MALTOSE (ANHYDROUS AND CRYSTALLISED).

(For Lactose Figures see pages 58 to 61.)—Continued.

(Expressed in milligrams.)

Cuprous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Dextrose (d-glu- cose)	Invert sugar	Invert sugar and saccharose		Maltose		Cuprous oxide (Cu <sub>2</sub> O)
				0.4 grm. total sugar	2 grm. total sugar	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> + H <sub>2</sub> O	
175	155.5	77.4	80.1	78.4	72.2	136.7	143.9	175
176	156.3	77.8	80.6	78.8	72.7	137.5	144.7	176
177	157.2	78.3	81.0	79.3	73.2	138.3	145.5	177
178	158.1	78.8	81.5	79.8	73.7	139.1	146.4	178
179	159.0	79.2	82.0	80.3	74.2	139.8	147.2	179
180	159.9	79.7	82.5	80.8	74.6	140.6	148.0	180
181	160.8	80.1	82.9	81.3	75.1	141.4	148.9	181
182	161.7	80.6	83.4	81.7	75.6	142.2	149.7	182
183	162.6	81.1	83.9	82.2	76.1	143.0	150.5	183
184	163.4	81.5	84.4	82.7	76.6	143.8	151.4	184
185	164.3	82.0	84.9	83.2	77.1	144.6	152.2	185
186	165.2	82.5	85.3	83.7	77.6	145.4	153.0	186
187	166.1	82.9	85.8	84.2	78.0	146.2	153.9	187
188	167.0	83.4	86.3	84.6	78.5	147.0	154.7	188
189	167.9	83.9	86.8	85.1	79.0	147.8	155.5	189
190	168.8	84.3	87.2	85.6	79.5	148.6	156.4	190
191	169.7	84.8	87.7	86.1	80.0	149.3	157.2	191
192	170.5	85.3	88.2	86.6	80.5	150.1	158.0	192
193	171.4	85.7	88.7	87.1	81.0	150.9	158.9	193
194	172.3	86.2	89.2	87.6	81.4	151.7	159.7	194
195	173.2	86.7	89.6	88.0	81.9	152.5	160.5	195
196	174.1	87.1	90.1	88.5	82.4	153.3	161.4	196
197	175.0	87.6	90.6	89.0	82.9	154.1	162.2	197
198	175.9	88.1	91.1	89.5	83.4	154.9	163.0	198
199	176.8	88.5	91.6	90.0	83.9	155.7	163.9	199
200	177.7	89.0	92.0	90.5	84.4	156.5	164.7	200
201	178.5	89.5	92.5	91.0	84.8	157.3	165.5	201
202	179.4	89.9	93.0	91.4	85.3	158.1	166.4	202
203	180.3	90.4	93.5	91.9	85.8	158.8	167.2	203
204	181.2	90.9	94.0	92.4	86.3	159.6	168.0	204
205	182.1	91.4	94.5	92.9	86.8	160.4	168.9	205
206	183.0	91.8	94.9	93.4	87.3	161.2	169.7	206
207	183.9	92.3	95.4	93.9	87.8	162.0	170.5	207
208	184.8	92.8	95.9	94.4	88.3	162.8	171.4	208
209	185.6	93.2	96.4	94.9	88.8	163.6	172.2	209
210	186.5	93.7	96.9	95.4	89.2	164.4	173.0	210
211	187.4	94.2	97.4	95.8	89.7	165.2	173.8	211
212	188.3	94.6	97.8	96.3	90.2	166.0	174.7	212
213	189.2	95.1	98.3	96.8	90.7	166.8	175.5	213
214	190.1	95.6	98.8	97.3	91.2	167.5	176.4	214
215	191.0	96.1	99.3	97.8	91.7	168.3	177.2	215
216	191.9	96.5	99.8	98.3	92.2	169.1	178.0	216
217	192.8	97.0	100.3	98.8	92.7	169.9	178.9	217
218	193.6	97.5	100.8	99.3	93.2	170.7	179.7	218
219	194.5	98.0	101.2	99.8	93.7	171.5	180.5	219
220	195.4	98.4	101.7	100.3	94.2	172.3	181.4	220
221	196.3	98.9	102.2	100.8	94.7	173.1	182.2	221
222	197.2	99.4	102.7	101.2	95.1	173.9	183.0	222
223	198.1	99.9	103.2	101.7	95.6	174.7	183.9	223
224	199.0	100.3	103.7	102.2	96.1	175.5	184.7	224
225	199.9	100.8	104.2	102.7	96.6	176.2	185.5	225
226	200.7	101.3	104.6	103.2	97.1	177.0	186.4	226
227	201.6	101.8	105.1	103.7	97.6	177.8	187.2	227
228	202.5	102.2	105.6	104.2	98.1	178.6	188.0	228
229	203.4	102.7	106.1	104.7	98.6	179.4	188.8	229

TABLE FOR CALCULATING DEXTROSE, INVERT SUGAR ALONE, INVERT SUGAR IN THE PRESENCE OF SACCHAROSE (0.4 GRM. AND 2 GRM. TOTAL SUGAR), LACTOSE (THREE FORMS), AND MALTOSE (ANHYDROUS AND CRYSTALLISED).

(For Lactose Figures see pages 58 to 61.)—Continued.

(Expressed in milligrams.)

Cuprous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Dextrose (d-glu- cose)	Invert sugar	Invert sugar and saccharose		Maltose		Cuprous oxide (Cu <sub>2</sub> O)
				0.4 grm. total sugar	2 grm. total sugar	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> + H <sub>2</sub> O	
230	204.3	103.2	106.6	105.2	99.1	180.2	189.7	230
231	205.2	103.7	107.1	105.7	99.6	181.0	190.5	231
232	206.1	104.1	107.6	106.2	100.1	181.8	191.3	232
233	207.0	104.6	108.1	106.7	100.6	182.6	192.2	233
234	207.9	105.1	108.6	107.2	101.1	183.4	193.0	234
235	208.7	105.6	109.1	107.7	101.6	184.2	193.8	235
236	209.6	106.0	109.5	108.2	102.1	184.9	194.7	236
237	210.5	106.5	110.0	108.7	102.6	185.7	195.5	237
238	211.4	107.0	110.5	109.2	103.1	186.5	196.3	238
239	212.3	107.5	111.0	109.6	103.5	187.3	197.2	239
240	213.2	108.0	111.5	110.1	104.0	188.1	198.0	240
241	214.1	108.4	112.0	110.6	104.5	188.9	198.8	241
242	215.0	108.9	112.5	111.1	105.0	189.7	199.7	242
243	215.8	109.4	113.0	111.6	105.5	190.5	200.5	243
244	216.7	109.9	113.5	112.1	106.0	191.3	201.3	244
245	217.6	110.4	114.0	112.6	106.5	192.1	202.2	245
246	218.5	110.8	114.5	113.1	107.0	192.9	203.0	246
247	219.4	111.3	115.0	113.6	107.5	193.6	203.8	247
248	220.3	111.8	115.4	114.1	108.0	194.4	204.7	248
249	221.2	112.3	115.9	114.6	108.5	195.2	205.5	249
250	222.1	112.8	116.4	115.1	109.0	196.0	206.3	250
251	223.0	113.2	116.9	115.6	109.5	196.8	207.2	251
252	223.8	113.7	117.4	116.1	110.0	197.6	208.0	252
253	224.7	114.2	117.9	116.6	110.5	198.4	208.8	253
254	225.6	114.7	118.4	117.1	111.0	199.2	209.7	254
255	226.5	115.2	118.9	117.6	111.5	200.0	210.5	255
256	227.4	115.7	119.4	118.1	112.0	200.8	211.3	256
257	228.3	116.1	119.9	118.6	112.5	201.6	212.2	257
258	229.2	116.6	120.4	119.1	113.0	202.3	213.0	258
259	230.1	117.1	120.9	119.6	113.5	203.1	213.8	259
260	231.0	117.6	121.4	120.1	114.0	203.9	214.7	260
261	231.8	118.1	121.9	120.6	114.5	204.7	215.5	261
262	232.7	118.6	122.4	121.1	115.0	205.5	216.3	262
263	233.6	119.0	122.9	121.6	115.5	206.3	217.2	263
264	234.5	119.5	123.4	122.1	116.0	207.1	218.0	264
265	235.4	120.0	123.9	122.6	116.5	207.9	218.8	265
266	236.3	120.5	124.4	123.1	117.0	208.7	219.7	266
267	237.2	121.0	124.9	123.6	117.5	209.5	220.5	267
268	238.1	121.5	125.4	124.1	118.0	210.3	221.3	268
269	238.9	122.0	125.9	124.6	118.5	211.0	222.1	269
270	239.8	122.5	126.4	125.1	119.0	211.8	223.0	270
271	240.7	122.9	126.9	125.6	119.5	212.6	223.8	271
272	241.6	123.4	127.4	126.2	120.0	213.4	224.6	272
273	242.5	123.9	127.9	126.7	120.6	214.2	225.5	273
274	243.4	124.4	128.4	127.2	121.1	215.0	226.3	274
275	244.3	124.9	128.9	127.7	121.6	215.8	227.1	275
276	245.2	125.4	129.4	128.2	122.1	216.6	228.0	276
277	246.1	125.9	129.9	128.7	122.6	217.4	228.8	277
278	246.9	126.4	130.4	129.2	123.1	218.2	229.6	278
279	247.8	126.9	130.9	129.7	123.6	218.9	230.5	279
280	248.7	127.3	131.4	130.2	124.1	219.7	231.3	280
281	249.6	127.8	131.9	130.7	124.6	220.5	232.1	281
282	250.5	128.3	132.4	131.2	125.1	221.3	233.0	282
283	251.4	128.8	132.9	131.7	125.6	222.1	233.8	283
284	252.3	129.3	133.4	132.2	126.1	222.9	234.6	284

**TABLE FOR CALCULATING DEXTROSE, INVERT SUGAR ALONE, INVERT SUGAR IN THE PRESENCE OF SACCHAROSE (0.4 GRM. AND 2 GRM. TOTAL SUGAR), LACTOSE (THREE FORMS), AND MALTOSE (ANHYDROUS AND CRYSTALLISED).**

(For Lactose Figures see pages 58 to 61.)—*Continued.*

(Expressed in milligrams.)

Cuprous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Dextrose (d-glu- cose)	Invert sugar	Invert sugar and saccharose		Maltose		Cuprous oxide (Cu <sub>2</sub> O)
				0.4 grm. total sugar	2 grm. total sugar	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> + H <sub>2</sub> O	
285	253.2	129.8	133.9	132.7	126.6	223.7	235.5	285
286	254.0	130.3	134.4	133.2	127.1	224.5	236.3	286
287	254.9	130.8	134.9	133.7	127.6	225.3	237.1	287
288	255.8	131.3	135.4	134.3	128.1	226.1	238.0	288
289	256.7	131.8	135.9	134.8	128.6	226.9	238.8	289
290	257.6	132.3	136.4	135.3	129.2	227.6	239.6	290
291	258.5	132.7	136.9	135.8	129.7	228.4	240.5	291
292	259.4	133.2	137.4	136.3	130.2	229.2	241.3	292
293	260.3	133.7	137.9	136.8	130.7	230.0	242.1	293
294	261.2	134.2	138.4	137.3	131.2	230.8	242.9	294
295	262.0	134.7	138.9	137.8	131.7	231.6	243.8	295
296	262.9	135.2	139.4	138.3	132.2	232.4	244.6	296
297	263.8	135.7	140.0	138.8	132.7	233.2	245.4	297
298	264.7	136.2	140.5	139.4	133.2	234.0	246.3	298
299	265.6	136.7	141.0	139.9	133.7	234.8	247.1	299
300	266.5	137.2	141.5	140.4	134.2	235.5	247.9	300
301	267.4	137.7	142.0	140.9	134.8	236.3	248.8	301
302	268.3	138.2	142.5	141.4	135.3	237.1	249.6	302
303	269.1	138.7	143.0	141.9	135.8	237.9	250.4	303
304	270.0	139.2	143.5	142.4	136.3	238.7	251.3	304
305	270.9	139.7	144.0	142.9	136.8	239.5	252.1	305
306	271.8	140.2	144.5	143.4	137.3	240.3	252.9	306
307	272.7	140.7	145.0	144.0	137.8	241.1	253.8	307
308	273.6	141.2	145.5	144.5	138.3	241.9	254.6	308
309	274.5	141.7	146.1	145.0	138.8	242.7	255.4	309
310	275.4	142.2	146.6	145.5	139.4	243.5	256.3	310
311	276.3	142.7	147.1	146.0	139.9	244.2	257.1	311
312	277.1	143.2	147.6	146.5	140.4	245.0	257.9	312
313	278.0	143.7	148.1	147.0	140.9	245.8	258.8	313
314	278.9	144.2	148.6	147.6	141.4	246.6	259.6	314
315	279.8	144.7	149.1	148.1	141.9	247.4	260.4	315
316	280.7	145.2	149.6	148.6	142.4	248.2	261.2	316
317	281.6	145.7	150.1	149.1	143.0	249.0	262.1	317
318	282.5	146.2	150.7	149.6	143.5	249.8	262.9	318
319	283.4	146.7	151.2	150.1	144.0	250.6	263.7	319
320	284.2	147.2	151.7	150.7	144.5	251.3	264.6	320
321	285.1	147.7	152.2	151.2	145.0	252.1	265.4	321
322	286.0	148.2	152.7	151.7	145.5	252.9	266.2	322
323	286.9	148.7	153.2	152.2	146.0	253.7	267.1	323
324	287.8	149.2	153.7	152.7	146.6	254.5	267.9	324
325	288.7	149.7	154.3	153.2	147.1	255.3	268.7	325
326	289.6	150.2	154.8	153.8	147.6	256.1	269.6	326
327	290.5	150.7	155.3	154.3	148.1	256.9	270.4	327
328	291.4	151.2	155.8	154.8	148.6	257.7	271.2	328
329	292.2	151.7	156.3	155.3	149.1	258.5	272.1	329
330	293.1	152.2	156.8	155.8	149.7	259.3	272.9	330
331	294.0	152.7	157.3	156.4	150.2	260.0	273.7	331
332	294.9	153.2	157.9	156.9	150.7	260.8	274.6	332
333	295.8	153.7	158.4	157.4	151.2	261.6	275.4	333
334	296.7	154.2	158.9	157.9	151.7	262.4	276.2	334
335	297.6	154.7	159.4	158.4	152.3	263.2	277.0	335
336	298.5	155.2	159.9	159.0	152.8	264.0	277.9	336
337	299.3	155.8	160.5	159.5	153.3	264.8	278.7	337
338	300.2	156.3	161.0	160.0	153.8	265.6	279.5	338
339	301.1	156.8	161.5	160.5	154.3	266.4	280.4	339

**TABLE FOR CALCULATING DEXTROSE, INVERT SUGAR ALONE, INVERT SUGAR IN THE PRESENCE OF SACCHAROSE (0.4 GRM. AND 2 GRM. TOTAL SUGAR), LACTOSE (THREE FORMS), AND MALTOSE (ANHYDROUS AND CRYSTALLISED).**

(For Lactose Figures see pages 58 to 61.)—*Continued.*

(Expressed in milligrams.)

Cuprous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Dextrose (d-glu- cose)	Invert sugar	Invert sugar and saccharose		Maltose		Cuprous oxide (Cu <sub>2</sub> O)
				0.4 grm. total sugar	2 grm. total sugar	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> + H <sub>2</sub> O	
340	302.0	157.3	162.0	161.0	154.8	267.1	281.2	340
341	302.9	157.8	162.5	161.6	155.4	267.9	282.0	341
342	303.8	158.3	163.1	162.1	155.9	268.7	282.9	342
343	304.7	158.8	163.6	162.6	156.4	269.5	283.7	343
344	305.6	159.3	164.1	163.1	156.9	270.3	284.5	344
345	306.5	159.8	164.6	163.7	157.5	271.1	285.4	354
346	307.3	160.3	165.1	164.2	158.0	271.9	286.2	346
347	308.2	160.8	165.7	164.7	158.5	272.7	287.0	347
348	309.1	161.4	166.2	165.2	159.0	273.5	287.9	348
349	310.0	161.9	166.7	165.7	159.5	274.3	288.7	349
350	310.9	162.4	167.2	166.3	160.1	275.0	289.5	350
351	311.8	162.9	167.7	166.8	160.6	275.8	290.4	351
352	312.7	163.4	168.3	167.3	161.1	276.6	291.2	352
353	313.6	163.9	168.8	167.8	161.6	277.4	292.0	353
354	314.4	164.4	169.3	168.4	162.2	278.2	292.8	354
355	315.3	164.9	169.8	168.9	162.7	279.0	293.7	355
356	316.2	165.4	170.4	169.4	163.2	279.8	294.5	356
357	317.1	166.0	170.9	170.0	163.7	280.6	295.3	357
358	318.0	166.5	171.4	170.5	164.3	281.4	296.2	358
359	318.9	167.0	171.9	171.0	164.8	282.2	297.0	359
360	319.8	167.5	172.5	171.5	165.3	282.9	297.8	360
361	320.7	168.0	173.0	172.1	165.8	283.7	298.7	361
362	321.6	168.5	173.5	172.6	166.4	284.5	299.5	362
363	322.4	169.0	174.0	173.1	166.9	285.3	300.3	363
364	323.3	169.6	174.6	173.7	167.4	286.1	301.8	364
365	324.2	170.1	175.1	174.2	167.9	286.9	302.0	365
366	325.1	170.6	175.6	174.7	168.5	287.7	302.8	366
367	326.0	171.1	176.1	175.2	169.0	288.5	303.6	367
368	326.9	171.6	176.7	175.8	169.5	289.3	304.5	368
369	327.8	172.1	177.2	176.3	170.0	290.0	305.3	369
370	328.7	172.7	177.7	176.8	170.6	290.8	306.1	370
371	329.5	173.2	178.3	177.4	171.1	291.6	307.0	371
372	330.4	173.7	178.8	177.9	171.6	292.4	307.8	372
373	331.3	174.2	179.3	178.4	172.2	293.2	308.6	373
374	332.2	174.7	179.8	179.0	172.7	294.0	309.5	374
375	333.1	175.3	180.4	179.5	173.2	294.8	310.3	375
376	334.0	175.8	180.9	180.0	173.7	295.6	311.1	376
377	334.9	176.3	181.4	180.6	174.3	296.4	312.0	377
378	335.8	176.8	182.0	181.1	174.8	297.2	312.8	378
379	336.7	177.3	182.5	181.6	175.3	297.9	313.6	379
380	337.5	177.9	183.0	182.1	175.9	298.7	314.5	380
381	338.4	178.4	183.6	182.7	176.4	299.5	315.3	381
382	339.3	178.9	184.1	183.2	176.9	300.3	316.1	382
383	340.2	179.4	184.6	183.8	177.5	301.1	316.9	383
384	341.1	180.0	185.2	184.3	178.0	301.9	317.8	384
385	342.0	180.5	185.7	184.8	178.5	302.7	318.6	385
386	342.9	181.0	186.2	185.4	179.1	303.5	319.4	386
387	343.8	181.5	186.8	185.9	179.6	304.2	320.3	387
388	344.6	182.0	187.3	186.4	180.1	305.0	321.1	388
389	345.5	182.6	187.8	187.0	180.6	305.8	321.9	389
390	346.4	183.1	188.4	187.5	181.2	306.6	322.8	390
391	347.3	183.6	188.9	188.0	181.7	307.4	323.6	391
392	348.2	184.1	189.4	188.6	182.3	308.2	324.4	392
393	349.1	184.7	190.0	189.1	182.8	309.0	325.2	393
394	350.0	185.2	190.5	189.7	183.3	309.8	326.1	394

TABLE FOR CALCULATING DEXTROSE, INVERT SUGAR ALONE, INVERT SUGAR IN THE PRESENCE OF SACCHAROSE (0.4 GRM. AND 2 GRM. TOTAL SUGAR), LACTOSE (THREE FORMS), AND MALTOSE (ANHYDROUS AND CRYSTALLISED).

(For Lactose Figures see pages 58 to 61.)—Continued.

(Expressed in milligrams.)

Cuprous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Dextrose (d-glu- cose)	Invert sugar	Invert sugar and saccharose		Maltose		Cuprous oxide (Cu <sub>2</sub> O)
				0.4 grm. total sugar	2 grm. total sugar	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> + H <sub>2</sub> O	
395	350.9	185.7	191.0	190.2	183.9	310.6	326.9	395
396	351.8	186.2	191.6	190.7	184.4	311.4	327.7	396
397	352.6	186.8	192.1	191.3	184.9	312.1	328.6	397
398	353.5	187.3	192.7	191.8	185.5	312.9	329.4	398
399	354.4	187.8	193.2	192.3	186.0	313.7	330.2	399
400	355.3	188.4	193.7	192.9	186.5	314.5	331.1	400
401	356.2	188.9	194.3	193.4	187.1	315.3	331.9	401
402	357.1	189.4	194.8	194.0	187.6	316.1	332.7	402
403	358.0	189.9	195.4	194.5	188.1	316.9	333.6	403
404	358.9	190.5	195.9	195.0	188.7	317.7	334.4	404
405	359.7	191.0	196.4	195.6	189.2	318.5	335.2	405
406	360.6	191.5	197.0	196.1	189.8	319.2	336.0	406
407	361.5	192.1	197.5	196.7	190.3	320.0	336.9	407
408	362.4	192.6	198.1	197.2	190.8	320.8	337.7	408
409	363.3	193.1	198.6	197.7	191.4	321.6	338.5	409
410	364.2	193.7	199.1	198.3	191.9	322.4	339.4	410
411	365.1	194.2	199.7	198.8	192.5	323.2	340.2	411
412	366.0	194.7	200.2	199.4	193.0	324.0	341.0	412
413	366.9	195.2	200.8	199.9	193.5	324.8	341.9	413
414	367.7	195.8	201.3	200.5	194.1	325.6	342.7	414
415	368.6	196.3	201.8	201.0	194.6	326.3	343.5	415
416	369.5	196.8	202.4	201.6	195.2	327.1	344.4	416
417	370.4	197.4	202.9	202.1	195.7	327.9	345.2	417
418	371.3	197.9	203.5	202.6	196.2	328.7	346.0	418
419	372.2	198.4	204.0	203.2	196.8	329.5	346.8	419
420	373.1	199.0	204.6	203.7	197.3	330.3	347.7	420
421	374.0	199.5	205.1	204.3	197.9	331.1	348.5	421
422	374.8	200.1	205.7	204.8	198.4	331.9	349.3	422
423	375.7	200.6	206.2	205.4	198.9	332.7	350.2	423
424	376.6	201.1	206.7	205.9	199.5	333.4	351.0	424
425	377.5	201.7	207.3	206.5	200.0	334.2	351.8	425
426	378.4	202.2	207.8	207.0	200.6	335.0	352.7	426
427	379.3	202.8	208.4	207.6	201.1	335.8	353.5	427
428	380.2	203.3	208.9	208.1	201.7	336.6	354.3	428
429	381.1	203.8	209.5	208.7	202.2	337.4	355.1	429
430	382.0	204.4	210.0	209.2	202.7	338.2	356.0	430
431	382.8	204.9	210.6	209.8	203.3	339.0	356.8	431
432	383.7	205.5	211.1	210.3	203.8	339.7	357.6	432
433	384.6	206.0	211.7	210.9	204.4	340.5	358.5	433
434	385.5	206.5	212.2	211.4	204.9	341.3	359.3	434
435	386.4	207.1	212.8	212.0	205.5	342.1	360.1	435
436	387.3	207.6	213.3	212.5	206.0	342.9	361.0	436
437	388.2	208.2	213.9	213.1	206.6	343.7	361.8	437
438	389.1	208.7	214.4	213.6	207.1	344.5	362.6	438
439	390.0	209.2	215.0	214.2	207.7	345.3	363.4	439
440	390.8	209.8	215.5	214.7	208.2	346.1	364.3	440
441	391.7	210.3	216.1	215.3	208.8	346.8	365.1	441
442	392.6	210.9	216.6	215.8	209.3	347.6	365.9	442
443	393.5	211.4	217.2	216.4	209.9	348.4	366.8	443
444	394.4	212.0	217.8	216.9	210.4	349.2	367.6	444
445	395.3	212.5	218.3	217.5	211.0	350.0	368.4	445
446	396.2	213.1	218.9	218.0	211.5	350.8	369.3	446
447	397.1	213.6	219.4	218.6	212.1	351.6	370.1	447
448	397.9	214.1	220.0	219.1	212.6	352.4	370.9	448
449	398.8	214.7	220.5	219.7	213.2	353.2	371.7	449



**TABLE FOR CALCULATING DEXTROSE, INVERT SUGAR ALONE, INVERT SUGAR IN THE PRESENCE OF SACCHAROSE (0.4 GRM. AND 2 GRM. TOTAL SUGAR), LACTOSE (THREE FORMS), AND MALTOSE (ANHYDROUS AND CRYSTALLISED).**

(For Lactose Figures see pages 58 to 61.)—*Continued.*

(Expressed in milligrams.)

Cuprous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Dextrose (d-glu- cose)	Invert sugar	Invert sugar and saccharose		Maltose		Cuprous oxide (Cu <sub>2</sub> O)
				0.4 gm. total sugar	2 gm. total sugar	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> + H <sub>2</sub> O	
450	399.7	215.2	221.1	220.2	213.7	353.9	372.6	450
451	400.6	215.8	221.6	220.8	214.3	354.7	373.4	451
452	401.5	216.3	222.2	221.4	214.8	355.5	374.2	452
453	402.4	216.9	222.8	221.9	215.4	356.3	375.1	453
454	403.3	217.4	223.3	222.5	215.9	357.1	375.9	454
455	404.2	218.0	223.9	223.0	216.5	357.9	376.7	455
456	405.1	218.5	224.4	223.6	217.0	358.7	377.6	456
457	405.9	219.1	225.0	224.1	217.6	359.5	378.4	457
458	406.8	219.6	225.5	224.7	218.1	360.3	379.2	458
459	407.7	220.2	226.1	225.3	218.7	361.0	380.0	459
460	408.6	220.7	226.7	225.8	219.2	361.8	380.9	460
461	409.5	221.3	227.2	226.4	219.8	362.6	381.7	461
462	410.4	221.8	227.8	226.9	220.3	363.4	382.5	462
463	411.3	222.4	228.3	227.5	220.9	364.2	383.4	463
464	412.2	222.9	228.9	228.1	221.4	365.0	384.2	464
465	413.0	223.5	229.5	228.6	222.0	365.8	385.0	465
466	413.9	224.0	230.0	229.2	222.5	366.6	385.9	466
467	414.8	224.6	230.6	229.7	223.1	367.3	386.7	467
468	415.7	225.1	231.2	230.3	223.7	368.1	387.5	468
469	416.6	225.7	231.7	230.9	224.2	368.9	388.3	469
470	417.5	226.2	232.3	231.4	224.8	369.7	389.2	470
471	418.4	226.8	232.8	232.0	225.3	370.5	390.0	471
472	419.3	227.4	233.4	232.5	225.9	371.3	390.8	472
473	420.2	227.9	234.0	233.1	226.4	372.1	391.7	473
474	421.0	228.5	234.5	233.7	227.0	372.9	392.5	474
475	421.9	229.0	235.1	234.2	227.6	373.7	393.3	475
476	422.8	229.6	235.7	234.8	228.1	374.4	394.2	476
477	423.7	230.1	236.2	235.4	228.7	375.2	395.0	477
478	424.6	230.7	236.8	235.9	229.2	376.0	395.8	478
479	425.5	231.3	237.4	236.5	229.8	376.8	396.6	479
480	426.4	231.8	237.9	237.1	230.3	377.6	397.5	480
481	427.3	232.4	238.5	237.6	230.9	378.4	398.3	481
482	428.1	232.9	239.1	238.2	231.5	379.2	399.1	482
483	429.0	233.5	239.6	238.8	232.0	380.0	400.0	483
484	429.9	234.1	240.2	239.3	232.6	380.7	400.8	484
485	430.8	234.6	240.8	239.9	233.2	381.5	401.6	485
486	431.7	235.2	241.4	240.5	233.7	382.3	402.4	486
487	432.6	235.7	241.9	241.0	234.3	383.1	403.3	487
488	433.5	236.3	242.5	241.6	234.8	383.9	404.1	488
489	434.4	236.9	243.1	242.2	235.4	384.7	404.9	489
490	435.3	237.4	243.6	242.7	236.0	385.5	405.8	490

**Remarks.**—It will be noticed that in this method it is recommended that the precipitate obtained should be weighed as cuprous oxide. This is undesirable for the reasons given on page 23, unless comparatively pure sugar solutions are being worked with. With the solutions obtained from ordinary plant products and from conversions by means of enzymes, etc., considerable error is undoubtedly incurred unless the copper is weighed as cupric oxide. The short time of heating is too, likely to cause error.



The writer can express no opinion as to the degree of accuracy of these tables but it may be pointed out, that it is extremely difficult to obtain pure maltose; all the so-called "pure" maltose on the market (Kahlbaum's, etc.) is indeed far from pure and in some cases contains 10 to 15% of dextrin. Such material can only be purified by repeated and laborious crystallisations (3 to 4 times) from 80% alcohol. The values given for maltose by Brown Morris and Millar (gravimetric) as well as those given by Ling and Jones (*infra*) (volumetric) can be relied upon.

**Volumetric Methods.**—Reasons are given on page 23 for considering that the method and tables due to Bertrand are not satisfactory for accurate work. On the other hand the volumetric method suggested by Ling (Vol. I, page 322<sup>1</sup>) is not only extremely rapid but is probably the most accurate volumetric method which has yet been suggested. The writer has thoroughly tested the tables given by Ling and Jones, using very carefully purified specimens of the different sugars, and can confirm the view generally held that this method is accurate to at least 1 part in 300 or 0.3%.

The following are the tables referred to. They refer to quantities of sugar solutions used to reduce 10 c.c. of Fehling solution, prepared as follows:

**Solution No. 1.**—Crystallised copper sulphate (69.2 gm.) is dissolved in water and the solution made up to 1 litre.

**Solution No. 2.**—Crystallised Rochelle salt (346 gm.) is dissolved in hot water and mixed with sodium hydroxide also dissolved in water (142 gm.). After cooling the mixed solutions are made up to 1 litre.

Equal volumes of these two solutions are accurately measured out at 15.5° (or any other standard temperature adopted) and this mixture constitutes the reagent. It is standardized as follows: Pure saccharose<sup>2</sup> (0.95 gm.) is dissolved in water (150 c.c.), and the solution boiled with 30 c.c. of *N*/2 hydrochloric acid exactly 1 minute; the solution is cooled, neutralised by adding *N*/2 sodium hydroxide (30 c.c.) and then diluted to 500 c.c. This solution, which contains 0.2 gm. of invert sugar per 100 c.c. is titrated against 10 c.c. portions of the copper reagent (see Allen, Vol. I, page 322).

The manner of using the table is best explained by an illustration. Suppose a solution of pure lævulose is being examined and that 25 c.c. of it are required to reduce 10 c.c. of Fehling's solution. Opposite 25 in the first column is found 0.2138 in column L; the percentage of lævulose in the solution titrated is thus given direct. If 25.2 c.c. or other quantity not a whole number is required to reduce 10 c.c. of Fehling's solution, the percentage of lævulose can easily be found by interpolation between the numbers given in column L.

The table gives the number of c.c. of Fehling's solution equivalent to 1 gm. of the particular sugar at each concentration. The numbers, given in columns D', L', I' and M' are used for another purpose—namely

<sup>1</sup> In Vol. I of Allen, page 322, line 6 from bottom, "2 seconds" should be 10 seconds.

<sup>2</sup> *Analyst*, 33, 160.

<sup>3</sup> See page 43.

TABLE III.—REDUCING POWER OF DIFFERENT SUGARS ACCORDING TO LING AND JONES.

Volume of solution required by 10 c.c. Fehling's solution	Dextrose		Lævulose		Invert sugar		Maltose	
	D Dextrose in 100 c.c. of solution	D' Fehling's solution equivalent to 1 grm. dextrose	L Lævulose in 100 c.c. of solution	L' Fehling's solution equivalent to 1 grm. lævulose	I Invert in 100 c.c. of solution	I' Fehling's solution equivalent to 1 grm. invert	M Maltose in 100 c.c. of solution.	M' Fehling's solution equivalent to 1 grm. maltose
C.c.	Gram.	C.c.	Gram.	C.c.	Gram.	C.c.	Gram.	C.c.
20	0.2427	206.0	.....	.....	.....	.....	.....	.....
21	0.2332	205.1	.....	.....	0.2412	197.5	0.3888	122.5
22	0.2226	204.2	0.2411	188.5	0.2311	196.8	0.3711	A constant
23	0.2138	203.4	0.2312	188.0	0.2218	196.0	0.3550	
24	0.2056	202.6	0.2222	187.5	0.2132	195.5	0.3402	
25	0.1981	201.9	0.2138	187.1	0.2052	194.9	0.3266	
26	0.1911	201.3	0.2060	186.7	0.1980	194.3	0.3140	
27	0.1846	200.7	0.1988	186.3	0.1910	193.9	0.3023	
28	0.1784	200.1	0.1921	186.0	0.1846	193.4	0.2915	
29	0.1728	199.6	0.1857	185.6	0.1787	193.0	0.2815	
30	0.1675	199.1	0.1798	185.4	0.1731	192.5	0.2721	
31	0.1625	198.6	0.1743	185.1	0.1678	192.2	0.2633	
32	0.1577	198.2	0.1691	184.8	0.1629	191.8	0.2551	
33	0.1532	197.8	0.1642	184.6	0.1583	191.5	0.2474	
34	0.1490	197.4	0.1596	184.3	0.1539	191.2	0.2401	
35	0.1450	197.0	0.1552	184.1	0.1497	190.9	0.2332	
36	0.1412	196.7	0.1511	183.9	0.1458	190.6	0.2268	
37	0.1377	196.4	0.1472	183.6	0.1421	190.3	0.2206	
38	0.1343	196.0	0.1435	183.4	0.1385	190.1	0.2148	
39	0.1310	195.8	0.1399	183.3	0.1349	189.8	0.2093	
40	0.1279	195.5	0.1366	183.1	0.1319	189.6	0.2041	122.5
41	.....	.....	0.1334	182.9	0.1288	189.4	.....	.....
42	.....	.....	0.1298	182.8	0.1259	189.2	.....	.....
43	.....	.....	0.1274	182.6	.....	.....	.....	.....

the separate determination of two reducing sugars in a mixture by a modification of Morris' method<sup>1</sup> (see pages 9 and 10).

**Estimation of Invert Sugar in Presence of Cane Sugar.**—Ling and Rendle (*Analyst*, 1908, 33, 170) have determined the corrections to be applied in order to allow for the influence of the saccharose when present in mixtures of sugars. In the following table IV:

Column A gives the amount in grams of saccharose present in 100 c.c. of the sugar solution.

Column B gives the percentage of saccharose present expressed on the total sugars.

Column C gives the percentage of invert sugar present expressed on the total sugars.

Column D gives the number of c.c. of sugar solution required to reduce 10 c.c. of Fehling's solution.

Column E gives the percentage of invert sugar on the total sugars found by direct experiment.

Column F gives the differences between the values shown in columns C and E.

The influence of the saccharose is seen to be practically negligible until the proportion to the total sugars (saccharose + invert sugar) amounts to 30%, at which point the invert sugar is overestimated by 0.2%. The in-

<sup>1</sup> *J. Inst. Brewing*, 4, 162.

TABLE IV.—EACH SOLUTION CONTAINED IN ADDITION TO THE SACCHAROSE SHOWN UNDER COLUMN A, 0.2 GRM. OF INVERT SUGAR PER 100 C.C.

A	B	C	D	E	F
0.01	4.8	95.2	25.60	95.30	0.10
0.03	13.0	87.0	25.60	87.10	0.10
0.05	20.0	80.0	25.60	80.10	0.10
0.10	33.3	66.7	25.55	66.90	0.20
0.20	50.0	50.0	25.45	50.40	0.40
0.30	60.0	40.0	25.40	40.40	0.40
0.40	66.6	33.4	25.35	33.80	0.40
0.50	71.4	28.6	25.30	29.00	0.40
0.60	75.0	25.0	25.20	25.40	0.40
0.70	77.7	22.3	25.15	22.70	0.40
0.80	80.0	20.0	25.10	20.40	0.40
1.25	86.2	13.8	25.05	14.10	0.30
1.50	88.2	11.8	24.95	12.10	0.30
1.75	89.7	10.3	24.85	10.60	0.30
1.75	89.7	10.3	24.80	10.60	0.30
2.00	90.9	9.1	24.70	9.45	0.35
2.00	90.9	9.1	24.80	9.41	0.31
2.50	92.5	7.5	24.80	7.76	0.26
3.00	93.8	6.2	24.70	6.44	0.24
5.00	96.1	3.9	24.20	4.05	0.15
7.00	97.2	2.8	23.60	3.04	0.24
10.00	98.0	2.0	22.95	2.23	0.23
20.00	99.0	1.0	22.40	1.14	0.14
25.00	99.2	0.8	22.25	0.92	0.12
30.00	99.3	0.7	22.25	0.80	0.10

fluence of the saccharose increases progressively until the proportion of the latter expressed on the total sugars is 99.3%, beyond which point it was not determined. At this point the invert sugar is overestimated by about 15%. It must be remembered that the magnitudes representing the percentages of invert sugar decrease as the percentage of saccharose increases, and the correction to be applied (column F) is in concrete numbers greatest when the percentage of saccharose in the total sugars is between 50 and 80%. In the case of a mixture of equal parts of saccharose and invert sugar the latter would be returned, if no correction were made, as 50.4 instead of 50.0%, whilst in the case of a mixture of 99 parts of saccharose and 1 of invert sugar the latter would be returned as 1.14% instead of 1.0%. Ling generally deducts the values shown in column F from the values ascertained by direct titration of the mixture of sugars. For this purpose it is necessary to know the percentage of saccharose not calculated on the sample, but on the total sugars (saccharose + invert sugar) in the sample. This can be determined by the Clerget method or by the method of double titration before and after hydrolysis with hydrochloric acid, applying the formula  $S = \frac{95I' - I}{100}$

in which S is the approximate percentage of saccharose, I the apparent percentage of invert sugar, *i.e.*, the value obtained by direct titration, and I' is the percentage of invert sugar obtained by titration after complete hydrolysis.

The approximate value given in column F is subtracted from the value of I and added to the value of S, the respective results giving the corrected percentages of invert sugar and of saccharose. In order to express these on the sample each of the values is multiplied by  $S + I/100$ . To be exact

the value added to the approximate percentage of saccharose, S, should be diminished by 5%; but the degree of accuracy of the method does not warrant this refinement, seeing that the corrections to be applied are comparatively small.

**Low's Volumetric Method** (Provisional A. O. A. C. Method).—In this method, the copper in the precipitate of cuprous oxide obtained by the action of a sugar solution on Fehling's solution is estimated iodometrically. The method prescribed by the A. O. A. C. is as follows (Bulletin 107, revised 1912, page 241):<sup>1</sup>

### LOW'S VOLUMETRIC METHOD, MODIFIED.<sup>2</sup> PROVISIONAL.

#### (a) Standardisation of the Thiosulphate Solution.

Prepare a solution of sodium thiosulphate containing 19 gm. of pure crystals to 1,000 c.c. Weigh accurately about 0.2 gm. of pure copper foil and place in a flask of 250 c.c. capacity. Dissolve by warming with 5 c.c. of a mixture of equal volumes of strong nitric acid and water. Dilute to 50 c.c., boil to expel the red fumes, add 5 c.c. of strong bromine water, and boil until the bromine is thoroughly expelled. Remove from the heat and add a slight excess of strong ammonium hydroxide—7 c.c. is about the right amount. Again boil until the excess of ammonia is expelled, as shown by a change of colour of the liquid and a partial precipitation. Now add a slight excess of strong acetic acid (3 or 4 c.c. of 80% acid) and boil for a minute. Cool to room temperature and add 10 c.c. of a solution of pure potassium iodide containing 300 gm. of potassium iodide to 1,000 c.c. Titrate at once with the thiosulphate solution until the brown tinge has become weak, then add sufficient starch liquor to produce a marked blue colouration. Continue the titration cautiously until the colour due to free iodine has entirely vanished. The blue colour changes toward the end to a faint lilac. If at this point the thiosulphate be added drop by drop and a little time be allowed for complete reaction after each addition, there is no difficulty in determining the end point within a single drop. 1 c.c. of the thiosulphate solution will be found to correspond to about 0.005 gm. of copper.

#### (b) Determination of Copper.

After washing the precipitated cuprous oxide, cover the Gooch with a watch glass and dissolve the oxide by means of 5 c.c. of warm nitric acid (1:1) poured under the watch glass with a pipette. Catch the filtrate in a flask of 250 c.c. capacity, wash the watch glass and Gooch free of copper; 50

<sup>1</sup> In a modification of the iodometric method suggested by Schoorl (*Zeit. angew. Chem.*, 1899, 633) the copper remaining in the Fehling's solution after treatment with the sugar solution is estimated and the difference between this value and that given by the Fehling's solution alone is a measure of the copper precipitate. This process obviates the necessity of filtering off the precipitate. Schoorl gives tables.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1902, 24, 1082.

c.c. of water will be sufficient. Boil to expel red fumes, add 5 c.c. of bromine water, boil off the bromine, and proceed exactly as in standardising the thiosulphate.

### **Estimation of Small Quantities of Reducing Sugars in Presence of a Large Quantity of Saccharose.**

It is well known that when large quantities of cane sugar are present, the values obtained for the reducing sugars, present in relatively small proportion, are considerably increased; this is probably due to the fact that, under the ordinary conditions of working, when the action takes place at the boiling point, traces of the saccharose are hydrolysed and so increase the actual amount of invert sugar present. Pellet<sup>1</sup> has made a special study of this question and points out that the amount of reduction obtained on heating Fehling's solution with solutions of cane sugar varies with: (1) the time of ebullition; (2) the proportion of Fehling's solution relative to the sugar; (3) the quantity of cane sugar; (4) the proportion of alkaline hydroxide in the Fehling's solution.

The effect of cane sugar on Fehling's solution according to Pellet is obviated by carrying out the heating, not at 100° as is usual, but at 60–62°; at this temperature there is not a trace of cuprous oxide formed when 10 gm. of pure cane sugar is heated for 10 minutes with 20 c.c. of Fehling's solution. Pellet suggests, therefore, the following process of estimating small quantities of reducing sugar in presence of large quantities of saccharose.

**Pellet's Method.**—The Fehling's solution used is prepared as follows:

Solution A. 34.64 gm. of copper sulphate made up to 500 c.c.

Solution B. Rochelle salt, 180 gm.  
Sodium hydroxide (sticks), 60 gm.

Water to make to 500 c.c.

This solution contains a relatively small proportion of sodium hydroxide and it may be noted, is very nearly the same in composition as that adopted by Brown, Morris and Millar (page 25). 10 c.c. of the mixed solution corresponds with 0.050 gm. of invert sugar.

To estimate the quantity of reducing sugar in highly purified and half-purified cane and beet products, 25 gm. of this material are dissolved in 100 c.c. of water; 20 c.c. of this solution is mixed with 20 c.c. of the Fehling's solution and 10 c.c. of water and the mixture heated in a beaker flask (see page 26) during 10 minutes in a water-bath at 60–62°. 50 c.c. of cold water are then added and the cuprous oxide collected at once, thoroughly washed and ignited to cupric oxide. Pellet makes use of a filter paper to collect the precipitate, in which case a blank experiment has to be made, with the same volume of Fehling's solution, in order to ascertain how much copper is taken up by the filter paper itself under exactly similar conditions.

<sup>1</sup> *Bull. Assoc. Chim. Sucr.*, 1913, 31, 182.

Pellet suggests using small filter papers having a diameter of about 3 cm. in conjunction with a special filtering arrangement devised for the purpose. With these small discs of filter paper the method can be used colourimetrically, the proportion of cuprous oxide being judged by the depth of colour on the disc of filter paper of known size; for this purpose a series of standards are prepared by means of known very small quantities of invert sugar. Under the conditions Pellet used, the weight of reducing sugar (invert sugar) is calculated by multiplying the weight of cupric oxide ( $\text{CuO}$ ) by 0.453. But the value of the constant will vary slightly according to the dimensions of the vessel in which the mixture of sugar and Fehling's solution is heated, that is, according to the proportion of the free surface to the depth, so that each worker should ascertain for himself the value of this ratio for his own conditions, by using a dilute solution of invert sugar (prepared from pure cane sugar) of known concentration.

Pellet states that by means of this method the true proportions of reducing sugar can be determined in even the highest grades of crystallised cane sugar, which are generally returned as free from invert sugar as they give less than 50 mg. of copper under the Herzfeld conditions (Vol. I, page 329) the generally unsatisfactory character of this method when used to estimate small quantities of invert sugar in cane sugar is shown by the fact that samples of pure saccharose, absolutely free from reducing sugar according to Pellet's method, will give as much as 100 mg. of cupric oxide when 10 grm. of the material are heated for 3 minutes with Fehling's solution at the boil. On the other hand, Pellet states that his method of working at  $60^\circ$  enables one readily to discriminate between sugars which are practically free from invert sugar and those which contain 0.01 or 0.02%. The exact quantity of the invert sugar in the latter cases can easily be estimated.

### Saccharose.

**Estimation by Inversion.**—In spite of the numerous researches which have been carried out during the past 20 years with the object of standardising the method of estimating cane sugar by inversion, it is now generally recognised that the Clerget-Herzfeld process is not entirely satisfactory in many cases. This is especially true of the estimation of saccharose in the mother liquors and molasses of sugar factories. In such cases, many possibilities of error arise. These have been recently summarised by H. Pellet in a monograph *Dosage du Sucre par Inversion* originally published in *La Sucrierie Indigène*, 1913, which forms a valuable survey of the whole question. The following is a brief summary of the principal sources of error in this method.

(1) It is necessary to make allowance for the change in the specific rotation of cane sugar caused by dilution. In the ordinary Clerget-Herzfeld formula the constant used, viz., 142.66 is correct only when the quan-



tity of cane sugar present is the half-normal weight, namely 13.0 grm.<sup>1</sup> In the case of products such as crude sugars and molasses, in which the actual sugar may be only 45%, it is necessary to use the constant which applies to the particular concentration of the saccharose actually present. This may be obtained from the following table, due to Herzfeld in 1888; or it can be determined directly by making a control observation with a solution of pure saccharose of approximately the same concentration as that present in the actual analysis. The latter method is really preferable because in this way any error in the instrument or in the graduation of vessels, etc., is allowed for.

TABLE V.  
ALTERATION OF HERZFELD CONSTANT WITH CONCENTRATION OF  
SACCHAROSE.

Grm. saccharose per 100 c.c.	Constant in Herzfeld formula	Grm. saccharose per 100 c.c.	Constant in Herzfeld formula
1	141.85	11	142.52
2	141.91	12	142.59
3	141.98	13	142.66
4	142.05	14	142.73
5	142.12	15	142.79
6	142.18	16	142.86
7	142.25	17	142.93
8	142.32	18	143.00
9	142.39	19	143.07
10	142.46	20	143.14

(2) The principal source of error in estimating sugars in beet molasses or in vegetable extracts in general, is due to the presence of amic acids or acid amides (such as glutamine, glutamic acid, asparagine and aspartic acids) which have a decided specific rotatory power; the error arises in the ordinary inversion process owing to the fact that such substances have a very different specific rotation in aqueous solution, in presence of basic lead acetate and in presence of hydrochloric acid. Pellet gives data for the amides named above, which show that in some cases, for example that of glutamic acid, a solution which is strongly lævorotatory in presence of a slight excess of basic lead acetate becomes strongly dextrorotatory when the solution is made acid. Consequently, the difference between the direct reading, taken in presence of basic lead acetate, and that obtained in acid solution, after inversion by the Herzfeld process, does not in such cases give a true measure of the cane sugar present; the change of rotation found is less than that actually due to the sugar present, which is consequently returned at a lower figure than is actually correct. There is also an error due to the transformation of an amide such as glutamine or asparagine into an acid such as glutamic acid, by partial hydrolysis, this change being accompanied by a change of rotation.

<sup>1</sup> Stanek (*Zeit. Zuckerind. Böhm.*, 1914, 38, 289), states that the constant 142.66, for this concentration, strictly holds good only when the inverted solution is polarised within 3 to 5 minutes; if the examination is delayed, as for instance, when the solution has to be decolourised, for 15 to 30 minutes the value 142.66 is too low, and the constant 143 should then be used.

Errors caused in this way by acid amides such as glutamine and asparagine (which are not eliminated by precipitation with basic lead acetate) are largely obviated by taking the *direct* polarisation reading in acid solution, according to Pellet's process (see below), using sulphurous acid instead of hydrochloric acid. This serves not only to remove the excess of lead by precipitation as sulphite, but at the same time clarifies and bleaches the solution so that it can easily be read in the polarimeter. The direct reading being taken in acid solution, is really comparable with the reading after inversion.

**Pellet's New Method of Estimating Saccharose in Molasses.**—100 gm. of the molasses are placed in a 500 c.c. flask together with water so as to make the volume equal to about 300 c.c.; after thoroughly mixing, basic lead acetate is gradually added until there is no further precipitate. This addition is made as carefully as possible so as to avoid having any considerable excess of the solution of lead. The solution, without filtering, is then diluted to 500 c.c., well shaken, and filtered. Take the *direct polarisation* of the filtrate (1).

Transfer 50 c.c. of the filtrate to a dry 100 c.c. measuring flask and make up to 100 c.c. with distilled water. If the measuring vessels, etc., are correct, the polarisation should be exactly half that formerly obtained. Another 50 c.c. of the filtrate are placed in a 100 c.c. flask and about 49 c.c. of sulphurous acid solution of sp. gr. 1.040 to 1.045 added<sup>1</sup> and the solution is diluted to 100 c.c. It is then carefully shaken, and 1 gm. of specially pure decolourising carbon (which must be without action on the sugars present) is added and the solution again agitated; it is then filtered and the polarisation observed, preferably in a 400 mm. tube. The result is multiplied by 0.9985, so as to take into account the volume of the precipitated lead sulphite. This gives the *acid direct polarisation* (2).

50 c.c. of the filtrate from the lead precipitate are placed in a 100 c.c. flask (A) with 5 c.c. of concentrated hydrochloric acid (sp. gr. 1.118) + 25 c.c. of sulphurous acid, sp. gr. 1.040 – 1.045. A second quantity is prepared similarly in a flask (B) and in a dried flask which serves as a temperature control, 80 c.c. of water are placed; all these flasks are then placed in a boiling water-bath, until the temperature of the control is exactly 70°; this is the case after 2½ to 3 minutes. The three flasks are then transferred to a water-bath heated at 70°, and flask A is heated 7 minutes and flask B 10 minutes at 70°. The extra 3 minutes heating in flask B ensures that inversion is complete and gives a check on the result obtained in flask A.

After the inversion the solutions A and B are cooled and diluted to 100 c.c. 1 gm. of pure decolourising carbon is added to each, the solutions are shaken, filtered and the polarisation taken (in a 400 mm. tube) (3). The cane sugar is calculated from the acid polarisation before inversion and the polarisation

<sup>1</sup> If one has sulphur-dioxide in siphon, it is sufficient to pass the gas through the 50 c.c. of solution for 2 to 3 minutes and then make up to 100 c.c. Ogilvie (*Int. Sugar J.*, 1912, 14, 624) showed that the original Pellet process gave a low figure for saccharose owing to an insufficiency of sulphur dioxide being used. With the modified process as given above, values are obtained which are identical with those obtained by invertase or by the Andriik method.



after inversion. Instead of using the usual constant 142.66, the value in Table V, which corresponds with the approximate quantity of sugar present should be employed.

**Use of Invertase in Estimating Saccharose.**—The use of the selective enzyme *invertase* has certain advantages in estimating cane sugar in complex mixtures such as molasses or the mixtures of sugars that are obtained on extracting leaves or other plant tissues. The enzyme brings about hydrolysis of cane sugar quite rapidly and completely at the ordinary temperature or slightly above it (the optimum temperature is 38°) and is purely selective in its action; it does not hydrolyse maltose or similar glucosides, and therefore is more discriminative in its action than hydrochloric acid under Herzfeld conditions. Ogilvie<sup>1</sup> has applied it to the analysis of beet and cane molasses and Davis and Daish<sup>2</sup> make use of it in the form of autolysed yeast (Vol. I, p. 314)<sup>3</sup> in their scheme of analysis of plant extracts (p. 64) following in this the example of Brown and Morris (*Trans.*, 1893, 63, 663). Ogilvie has shown that invertase gives practically the same results for molasses as Pellet's sulphurous acid method and both values are in close agreement with the values found by the Andrlik method<sup>4</sup> in which hydrochloric acid is used and urea is added to stop the invertive action of the acid on the cane sugar.

TABLE VI.—CANE MOLASSES.

	Cuban molasses		Egyptian molasses	Javan molasses	American syrup
	No. 1	No. 2			
Ash (sulphated).....	6.77	7.34	10.92	10.97	6.05
Reducing sugars.....	18.71	18.56	11.70	21.98	26.55
1. Alkaline (basic lead acetate) polarisation...	32.20	31.40	39.50	34.30	39.70
2. Neutral direct polarisation.....	30.50	29.90	38.10	33.46	39.65
3. Acid (HCl+urea) polarisation (Andrlik)...	30.50	30.50	38.40	33.38	39.26
4. Acid (SO <sub>2</sub> ) direct polarisation (Pellet).....	30.60	30.50	38.30	33.30	39.10
5. Invertase inversion polarisation.....	-16.40	-15.50	-17.90	-14.08	-11.40
6. Acid inversion (Herzfeld) polarisation.....	-16.30	-15.40	-18.02	-14.06	-12.28
7. % saccharose, using invertase.....	35.6	34.40	42.4	36.1	38.7
8. % saccharose using acid as hydrolyst and the alkaline direct polarisation.	36.7	35.40	43.4	36.6	39.3
9. % Saccharose using acid as hydrolyst and the neutral direct polarisation.	35.4	34.2	42.4	35.9	39.2
10. % saccharose using acid as hydrolyst and (HCl+urea) direct polarisation (Andrlik).	35.4	34.7	42.6	35.9	38.9
11. Saccharose, using acid as hydrolyst and (SO <sub>2</sub> ) direct polarisation (Pellet).	35.5	34.7	42.5	35.8	38.8

<sup>1</sup> *Int. Sugar J.*, 1912, 14, 89 and 624.

<sup>2</sup> *J. Agric. Sci.*, 1913, 5, 437.

<sup>3</sup> Hudson and Paine (*J. Amer. Chem. Soc.*, 1914, 36, 1566) have recently described a rather tedious method of preparing an invertase solution for cane sugar inversions, in which the solution from the autolysed yeast is clarified with lead acetate, the excess of lead removed with hydrogen sulphide and the liquid dialysed through a collodion sac in running water. This treatment is quite unnecessary to prevent the solution from undergoing change and also involves considerable loss of activity of the invertase preparation. A solution prepared in the following way can be kept 2 or 3 years without appreciably losing its activity. About ½ lb. of fresh brewer's yeast, after being thoroughly washed with water in a Buchner funnel to remove wort, is packed into a wide-necked bottle and, after adding about 50 c.c. of toluene is left to undergo autolysis for several days at about 38°; the yeast nearly completely liquefies, and the liquid, which is only very slightly coloured, is filtered from the solid residue. It is kept in a stoppered bottle in the dark. About 10 to 20 c.c. of toluene should be added, so as to keep a film of this liquid floating on the surface of the preparation and exclude air.

<sup>4</sup> *Zeit. Zuckerind. Böhm.*, 1906, 31, 417.

TABLE VII.—BEET MOLASSES.

(Ogilvie, *J. Soc. Chem. Ind.*, 1911, 30, 62.)

	Sample 1	Sample 2	Sample 3	Sample 4
1. Direct alkaline (basic lead) polarisation.....	48.8	.....	48.6	47.0
2. Direct neutral polarisation.....	49.2	52.0	49.0	47.6
3. Direct acid (Andrlik) polarisation.....	50.4	53.25	50.0	48.4
4. Direct acid (SO <sub>2</sub> ) polarisation (Pellet).....	50.3	53.3	.....	48.3
5. Invertase inversion polarisation.....	-14.6	-16.0	-15.0	-14.4
6. Acid inversion polarisation.....	-13.2	-14.6	-13.6	-13.8
7. Clerget value by invertase.....	48.5	51.7	48.6	47.1
8. Clerget value by acid, using alkaline direct polarisation.	47.0	.....	47.1	46.1
9. Clerget value by acid, using neutral direct polarisation.	47.3	50.5	47.4	46.5
10. Clerget value by acid, using acid (Andrlik) direct polarisation.	48.2	51.4	48.2	47.1
11. Clerget value by acid, using acid (SO <sub>2</sub> ) direct polarisation (Pellet).	48.1	51.4	.....	47.0

From these tables it is seen that with *beet* molasses the results obtained by the ordinary Herzfeld process using the alkaline direct polarisation are *low* as compared with the practically identical values obtained using invertase or the direct acid polarisation. In the case of *cane* molasses the reverse is true, the results obtained by the ordinary method being *high*. The difference is probably due to the different character of the disturbing factor in the two cases: in beet molasses it is the presence of amides and amino-acids and in cane molasses it is the reducing sugars.

According to Cross and Taggart<sup>1</sup> the retarding action of betaine and urea on the inversion of saccharose by hydrochloric acid is only slight at temperatures of 20 to 28° and therefore analytical methods based on this supposed retarding influence, such as the Andrlik process are not satisfactory. According to Pellet (*loc. cit.*) in the Andrlik method the polarisation of the acid solution should be completed in less than 7 minutes if change of the saccharose is to be avoided.

There is perhaps still some doubt whether the values obtained by the Pellet and Andrlik processes actually represent the true saccharose present; the agreement between the results obtained by the two methods may be fortuitous and it is worthy of note that the original Pellet method, in which a smaller proportion of sulphur dioxide was used, gave slightly different results and has been modified by increasing the amount of sulphur dioxide present. On the other hand, it is a confirmation of some value that the invertase method gives practically identical results (Ogilvie). It would, however, be interesting to ascertain whether the results obtained for cane sugar in such cases, by measuring the increase of reducing power by Fehling's solution (gravimetrically or volumetrically), correspond with those given by the change of rotation measured under the various conditions given above. Owing to the great influence of salts, acids and neutral substances such as betaine or urea on the specific rotatory power of the sugars and other optic-

<sup>1</sup> *Louisiana State University Agriculture Bulletin*, No. 135, December, 1912.

ally active substances present, a certain amount of doubt must be felt as to the strict reliability of methods which rest on the polarisation figures only, until it has been finally put beyond question by other methods that these are correct.

**Inversion of Saccharose by Citric Acid.**—In estimating saccharose in plant extracts it is inadvisable to invert with hydrochloric acid at  $70^{\circ}$  under Herzfeld conditions as if maltose is present a certain proportion undergoes hydrolysis to dextrose.<sup>1</sup> In such cases a weaker acid such as citric acid can be applied but error may arise unless special precautions are taken. Davis and Daish<sup>2</sup> show that in a series of experiments carried out on mangold leaf extracts from which tannins, amino-acids, etc., had been as far as possible removed by basic lead acetate in the usual way, the amount of cane sugar found by inverting with 2% citric acid was very small as compared with the amount found by means of invertase. It was ultimately discovered that the cause of the difference was the presence in solution of a relatively large proportion of sodium acetate, which almost entirely inhibits the invertive action of 2% citric acid. The sodium acetate was produced owing to the necessity, in the cases dealt with, of using relatively large quantities of basic lead acetate to remove the tannins, etc., present in the extracts analysed; on subsequently adding sodium carbonate to precipitate the slight excess of lead present in the filtered solution the whole of the acetic acid originally present in the basic acid acetate was converted into sodium acetate. It is an interesting fact that although sodium acetate, when present to the extent of about 1 to 2%, almost completely inhibits inversion of cane sugar by boiling 2% citric acid, it does not in the least interfere with the action of invertase (autolysed yeast); this shows the advantage of using invertase in many cases as a means of checking the results obtained by acid hydrolysis. The writer in estimating cane sugar in plant material invariably uses two methods (see page 65): (1) hydrolysis by boiling 10% citric acid; (2) hydrolysis during 24 hours at  $38^{\circ}$  by 1 c.c. of autolysed yeast (see footnote on page 46). The results mutually check each other. The method of carrying out the hydrolysis by 10% citric acid is as follows: 50 c.c. of the solution to be analysed (which has had the excess of lead removed by means of sodium carbonate) is treated with a few drops of concentrated sulphuric acid until it just shows the faintest indication of pink to methyl-orange. Solid citric acid is then added so as to make a 10% solution (5 grm. solid citric acid to 50 c.c. of solution) and the mixture raised to the boil; it is kept actively boiling over a small flame for 10 minutes, under a reflux condenser, and the solution is then cooled to the ordinary temperature and exactly neutralised (using phenolphthalein as indicator) by adding a 10 or 15% solution

<sup>1</sup> It is generally stated that maltose is not hydrolysed at all by hydrochloric acid under Herzfeld conditions and Kluyver (*Biochemische Suikerbepalingen*, 1914, page 223) considered that Davis and Daish were in error in considering this statement to be incorrect; the writer has however since shown (Davis, *J. Agric. Sci.*, 1914, 6, 413) that under Herzfeld conditions the hydrolysis of maltose is quite appreciable and sufficient to interfere with the accuracy of the cane sugar estimation.

<sup>2</sup> *J. Agric. Sci.*, 1913, 5, 437.

of sodium hydroxide. It is diluted to 100 c.c. at 15° (or 20° according to the temperature at which the flask is graduated) and is then ready for the polarisation or for measuring the reducing power by means of Fehling's solution.

In all cases that the writer has yet met, 10% citric acid under the conditions given has effected complete hydrolysis of the cane sugar even when very large quantities of basic lead acetate have been employed in the preliminary purification of the solutions dealt with. Special experiments have shown that no maltose is hydrolysed under these conditions.

**Influence of Basic Lead Acetate in Sugar Analysis.**—It has been generally considered since the work of Gill,<sup>1</sup> Pellet,<sup>2</sup> Edson,<sup>3</sup> and Geerligs<sup>4</sup> that when basic lead acetate is used in purifying and decolorising solutions containing reducing sugars, a considerable proportion of the latter is thrown out of solution; this action is most marked in the case of lævulose and Pellet has stated that in some cases 23% of the lævulose present is precipitated at the ordinary temperature, whilst at 50° this sugar is totally removed. Whilst the experimental results recorded by the above authors are perfectly correct, the writer, from a series of experiments as yet unpublished, has reason to doubt the correctness of the view that lævulose is precipitated under the conditions named above. It has been found that, at least in dilute solutions, lævulose is not *precipitated* at all by basic lead acetate, even in presence of impurities such as sodium sulphate or organic acids, and that no loss occurs *unless the solution of the lævulose is left in contact with the basic lead acetate for some time*. If to the solution containing the lævulose, basic lead acetate is added in not too large excess (5 c.c. or 10 c.c.) and then the lead is precipitated immediately by sodium sulphate or sodium carbonate, practically 100% of the lævulose is recovered in the solution. On the other hand, if the lævulose is left with the basic lead acetate for various lengths of time, for example, 1 hour, 24 hours, 48 hours, and the lead is subsequently precipitated by the same reagents, different proportions of sugar are found to have disappeared; the amount apparently lost increases with the time that the solution has been standing in contact with the basic lead acetate. At the same time the lævulose solution progressively becomes more and more yellow in colour, without, however, any precipitation becoming visible. It would appear that, instead of the lævulose being precipitated in the form of an insoluble lead compound, as has been generally supposed to be the case, what happens is that the lævulose is either destroyed by the basic lead acetate (possibly by an oxidising action which occurs in the alkaline solution) or it is transformed into another carbohydrate with a different specific rotatory power and a smaller reducing power. Lobry de Bruyn and

<sup>1</sup> *J. Chem., Soc.*, 1871, 24, 91.

<sup>2</sup> *Bull. Assoc. Chim. Sucr.*, 1891, 9, 439.

<sup>3</sup> *Zeitsch. Ver. Zuckerind.*, 40, 1037.

<sup>4</sup> *D. Zuckerind.*, 23, 1753.

van Ekenstein<sup>1</sup> by the action of lead hydroxide on lævulose isolated a hexose,  $C_6H_{12}O_6$ , to which they gave the name *glucose*; it has practically no action on the plane of polarised light and is not fermentable by yeast.

The higher the temperature the more rapid is the disappearance of lævulose, so that heating a solution containing reducing sugars with basic lead acetate must always be avoided.

It is well known that Pellet<sup>2</sup> advocates the use of neutral lead acetate in place of the basic lead acetate in clarifying liquors which contain reducing sugars, owing to the supposed precipitating effect of the basic salt on the lævulose. But in the majority of cases the neutral lead acetate is far less effective as a clarifying agent and, in the case of plant material, frequently leaves in solution optically active substances (for example gums) which are thrown down by the basic salt and therefore prevented from interfering with the analysis. From the results obtained by the writer it would appear that if the basic lead acetate is added carefully in small quantities at a time until the precipitation of the impurities is *just* complete,<sup>3</sup> and if the actual excess of basic lead acetate is not allowed to exceed about 5 c.c. on 300 to 500 c.c. of solution, there is practically *no loss whatever of lævulose*, or other reducing sugars. Direct experiment with mixtures of pure reducing sugars and tannin have shown that if care be taken *to avoid any considerable excess of basic lead acetate during the precipitation*, there is no loss of reducing sugars when the tannin is precipitated in this way. Parkin<sup>4</sup> cites a case of this kind when the following results were obtained in a test analysis:

	Tannin added and precipitated by 5 c.c. basic lead acetate	Control in distilled water
Saccharose.....	0.487	0.489
Dextrose.....	0.204	0.201
Lævulose.....	0.244	0.244
Total sugar.....	0.935	0.934

In this case, tannin was added to the solution just to the extent that it was all carried down in the precipitate caused by the addition of 5 c.c. of the basic lead solution; the excess of lead was not removed, and it is seen that this slight excess has had no influence on the result.

In agreement with the view the writer puts forward that no loss of lævulose ever occurs by actual precipitation, but that when such appears to take place it is usually caused by a transformation of the sugar by the alkaline lead solution, are the facts recently recorded by Le Docte.<sup>5</sup> The latter shows that whereas in carrying out the hot aqueous digestion process of extracting sugars in presence of basic lead acetate the polarisation due to lævulose (which was purposely added) *disappears* entirely, it is not changed at

<sup>1</sup> *Rec. Trav. Chim.*, 16, 262.

<sup>2</sup> *J. Fab. Sucre.*, 1899, 40, No. 15; *Bull. Assoc. Chim. Sucre.*, 1896, 15, 605; 1897, 16, 1007 and 1147; 1904, 22, 744; 1913, 31, 205; 1914, 32, 909.

<sup>3</sup> It is usually quite easy by making tests of small portions of the filtrate to hit off the point at which this occurs within 1 or 2 c.c., even when relatively large quantities (for example 100 to 300 c.c. of basic lead acetate have to be employed.

<sup>4</sup> *Biochem. J.*, 1911, 6, 12.

<sup>5</sup> *Sucrierie Belge*, 1912, 275.



all or changed only very slightly when the digestion is effected in the cold. Similarly when the actual hot digestion is carried out in the absence of basic lead acetate, and the latter is then added *after cooling*, the polarisation due to lævulose (or dextrose) is not in the least interfered with. It is concluded that, as stated above, when reducing sugars are present basic lead acetate should never be added to the hot solution.

Lævulose is far more sensitive to the action of basic lead acetate in the cold than dextrose or other sugars just as it is in general far more easily decomposed than these (compare page 53, action of hydrochloric acid). The writer finds that dextrose and maltose remain practically unchanged in presence of considerable excess of basic lead acetate and Le Docte (*loc. cit.*) also states that in presence of dextrose, the hot digestion with basic lead acetate can be carried out without loss of the reducing sugar. The fact that no precipitation or loss of either dextrose or maltose occurs in presence of basic lead acetate greatly simplifies the analysis in the case of solutions containing these substances. The writer has shown, for example,<sup>1</sup> that basic lead acetate can be used in removing impurities in the estimation of starch by means of taka-diastrase (see page 74), which converts the starch quantitatively into a mixture of maltose and dextrose, without any loss whatever occurring of either of these sugars.

In sugar analysis any considerable excess of basic lead acetate should always be avoided, and, in the majority of cases, any such excess should be removed before taking the actual polarisation readings, either by means of sulphurous acid as recommended by Pellet or by sodium carbonate, sodium sulphate, etc. If any excess of basic lead acetate is left it combines with the reducing sugars (dextrose, lævulose, maltose) forming *soluble* lead compounds which have an entirely different rotation from the sugars themselves; this is particularly the case with lævulose (or invert sugar) the negative rotation of which may become positive in presence of excess of basic lead acetate.

**Incomplete Inversion caused by the use of Large Quantities of Basic Lead Acetate or by the Presence of Salts of Organic Acids.**—In the ordinary analysis of sugar works materials and products the quantity of basic lead acetate used is generally relatively small and as much as 5 c.c. of the lead solution can be present in excess without interfering with the completeness of the inversion under Herzfeld conditions (see Pellet, *Dosage du Sucre*, page 39). On the other hand, in working with vegetable extracts, when much larger quantities of basic lead acetate have to be used, the proportion of lead which remains unprecipitated in the solution may be so great as to lead to incomplete inversion if only the usual quantity of hydrochloric acid is employed in the Herzfeld method; even if this lead be precipitated by sodium carbonate or sulphate, sodium acetate is formed, which inhibits more or less completely, the invertive action of the hydrochloric acid

<sup>1</sup> *J. Agric. Sci.*, 1914, 6, 152.

just as it does that of citric acid (see page 48). In such cases serious error in the analysis may arise and Pellet cites an instance (Private Communication) in which 6% of raffinose was returned as being present in a wild beet from this cause. Care should be taken in such cases to make the solution very faintly acid to methyl-orange by the addition of sulphuric or hydrochloric acid before adding the quantity of acid (5 c.c.) required under Herzfeld conditions. Duplicate experiments can also be profitably made in which the period of heating is prolonged to 10 or 15 minutes; Pellet has shown that under Herzfeld conditions the time of heating can be prolonged to 20 minutes (at 70°) without affecting the accuracy of the results; on the other hand, it is not desirable to increase the quantity of hydrochloric acid used to 10 c.c., as the extra proportion of acid used sensibly modifies the rotatory power of the invert sugar present.

When working with plant material or plant extracts, in the purification of which relatively large quantities of basic lead acetate have been employed, it is always advisable to carry out a control estimation of the cane sugar by means of invertase, inversion by which is complete even when sodium acetate is present in considerable quantity. It must be noted that if maltose is present, there is risk of bringing about considerable hydrolysis of this sugar to dextrose, if the time of heating be prolonged, under the Herzfeld conditions by 5 minutes. Even with 5 minutes heating, as pointed out on page 48, marked hydrolysis occurs, so that when maltose (or similar glucosides) are present it is advisable to use citric acid for the inversion under the conditions already defined (page 48).

**Estimation of Raffinose.**—In Vol. I, page 313 the Creydt formula

$$S = \frac{0.5188 P - I}{0.8454}$$

is given; this is still official in the United States (*Bulletin 107 (revised)*, 1912), but in Europe Herzfeld's later formula

$$S = \frac{0.5124 P - (-I)}{0.839}, \quad R = \frac{P - S}{1.85}$$

is more generally adopted.

The use of this method, however, in the case of vegetable material and beet molasses may return as raffinose numbers which are far from representing the true proportion of this substance present. This is due to the presence of other optically active substances, such as the glutamic and aspartic amides, the specific rotation of which undergoes a considerable change during the process of inversion. Pellet (*Dosage du Sucre*, page 63) gives an example of a crude sugar, showing a direct polarisation of 91.10 by the ordinary method (in presence of basic lead acetate) which, when examined according to the Herzfeld method, appeared to contain 0.5% of raffinose;

when, however, the direct polarisation was taken in presence of acid, the value found was 91.55 and the conclusion drawn was that no raffinose was actually present. Other sources of error in the estimation of raffinose may be incomplete inversion of the cane sugar owing to the presence of basic lead or sodium acetate (page 51), the presence of pentoses, etc.

From the above considerations it is clear that the estimation of raffinose by the ordinary method, now in general use, gives results upon which in the majority of cases little reliance can be placed.

### Estimation of Maltose.

As stated on page 24, Wein's tables showing the reducing power of maltose give results which are 5% low.

It has been frequently proposed to estimate maltose by hydrolysis with dilute hydrochloric or sulphuric acid at 100°, noting the change of cupric reducing power or specific rotatory power of the solution after allowing for the inversion of cane sugar present. Under carefully regulated conditions this method gives approximate results in the case of pure maltose or a mixture of maltose and dextrose (cf. Baker and Dick<sup>1</sup>) but, as shown by Davis and Daish<sup>2</sup> it is quite useless when saccharose or lævulose are also present, owing to the large amount of decomposition of the latter sugar which is caused by the prolonged heating with dilute acids. In the paper cited, it is shown that it is impossible to effect complete hydrolysis of maltose by dilute acid at 100°, without at the same time destroying a large proportion of the lævulose which is present; thus 31% of the lævulose present in a 1% solution is destroyed when this solution is heated with 2.4% hydrochloric acid during 2 hours, this being the time necessary to effect 98% of complete hydrolysis of maltose in a 1 per cent. solution of this sugar. Even at 70° it is impossible completely to hydrolyse maltose in presence of cane sugar or lævulose without at the same time destroying considerable quantities of lævulose; thus in 1% solution of the sugar, even after 24 hours' heating with a 2.4% solution of hydrochloric acid only 94% of the maltose is hydrolysed, whilst more than 5% of the lævulose is destroyed.

It is therefore impossible to estimate maltose with any degree of accuracy by acid hydrolysis when cane sugar or lævulose are also present. In such cases it is necessary to employ a biochemical method, involving the use of maltase-free yeasts. Davis and Daish (*loc. cit.*) have suggested the following process, which has been thoroughly tested and found to give quite accurate results; it was shown that it is possible to ferment away every trace of dextrose, lævulose, or cane sugar by means of any one of the three special yeasts *Saccharomyces marxianus*, *S. exiguus*, or *S. anomalus* and to recover every trace

<sup>1</sup> *Analyst*, 1905, 30, 79.

<sup>2</sup> *J. Agric. Sci.*, 1913, 5, 453.



of maltose, which can then be estimated by measuring the residual reducing power.

To 50 c.c. of the solution containing the sugars (previously purified by means of basic lead acetate and then freed from lead as described below) which must be very faintly acid to litmus paper, 5 c.c. of yeast water is added; the solution is then sterilised in a flask closed with a cotton-wool stopper, by heating during 20 minutes in the autoclave at 115–120°, and is then inoculated with a trace of the pure maltase-free yeast and incubated at 25° for 3 to 4 weeks. When the fermentation is complete<sup>1</sup> 5 c.c. of alumina cream are added and the solution well boiled; it is then filtered and the precipitate well washed until the filtrate has a volume of 100 c.c. An aliquot portion (50 c.c.) can then be used for measuring the reducing power.

For the yeasts to grow satisfactorily it is necessary to make sure that every trace of lead has been removed from the solution. The best method of effecting this is to throw down the excess of lead by adding sodium carbonate, little by little until no further precipitate is produced, then to make the filtrate slightly acid with hydrochloric acid and to precipitate the traces of lead remaining in solution by hydrogen sulphide. The lead can also be removed directly from the solution by using hydrogen sulphide without the prior employment of sodium carbonate, but in such cases the solution usually becomes strongly acid if much lead acetate be present (owing to the liberation of acetic acid) and this acidity must be very nearly neutralised by adding sodium carbonate before sterilising and inoculating with the yeast. In all cases, hydrogen sulphide is expelled by sucking air through the solution obtained after filtering from the lead sulphide; the solution which is used for the fermentations should show a faint but distinct acid indication to litmus.

When small quantities of pentoses are present in the solutions to be analysed (as is frequently the case in dealing with plant extracts) it is necessary to introduce a correction for these; the pentoses are very slowly, if at all, fermented by the maltase-free yeasts and consequently, like maltose itself, exercise a reducing effect on the Fehling solution. The correction for the pentoses is obtained by carrying out fermentations with a pure culture of ordinary distillery or brewers' yeast which ferments away the maltose but leaves the pentoses; the slight residual reducing power found after carrying out a fermentation with such yeast is indeed a measure of the pentoses present and can be used as a means of verifying the presence of these substances or of estimating them in cases when the ordinary pentose method is likely to give incorrect results owing to the presence of other sugars (Davis and Sawyer).<sup>2</sup> On subtracting the value found for the reducing power remaining after fermentation with ordinary yeast from the value given by the maltase-free yeasts, the cupric reduction due to the maltose alone is obtained.

<sup>1</sup> 0.20 to 0.5 grm. of cane sugar are invariably completely fermented under the above conditions after 3 weeks.

<sup>2</sup> *J. Agric. Sci.*, 1914, 6, 406.

During the past three years the writer has used this method of estimating maltose in more than 500 analyses of various kinds of plant material (plant extracts, germinated and ungerminated grain, starch conversions, etc.). It has been our custom to carry out five fermentations with each solution to be analysed, viz., one each with *S. anomalus*, *S. exiguus*, and *S. marxianus*, and two with distillery yeast. The agreement between the results with the different special yeasts has generally been entirely satisfactory. *S. anomalus* does not lend itself quite so well to quantitative experiments as the other maltase-free yeasts, as it is slower in its action and is less efficient as a sugar-remover—that is, a greater growth of yeast is necessary for the removal of a certain weight of sugar. Moreover, the Fehling solution in the subsequent reduction often filters very slowly and the cuprous oxide is also generally somewhat contaminated by traces of copper compounds formed by the action of the Fehling solution on substances elaborated during the growth of the yeast. It is therefore best to make use of *S. exiguus* and *S. marxianus* only. On page 64 is given a general scheme for the analysis of plant material, showing the way in which this method is applied in such cases.

**Biochemical Methods of Estimating Sugars.**—The estimation of maltose in the presence of other sugars dealt with above is an instance in which the ordinary chemical processes of sugar estimation are entirely useless and in which biochemical methods have to be employed. Kluyver has independently applied somewhat similar principles, with considerable success, to the estimation of the different constituent sugars present in complex mixtures of sugars, for example of maltose, saccharose, raffinose, with the simple hexoses. Full details are given in the monograph *Biochemische Suikerbepalingen* (Leiden, E. J. Brill, 1914. Kluyver makes use of a gasometric method, measuring the volume of carbon dioxide evolved by the action of a series of special yeasts and torulæ upon the solution dealt with; this method has the advantage that approximately accurate results are obtained with exceedingly small quantities of the solutions or sugar dealt with. A special eudiometer was devised in which the fermentation is carried out and the gas measured. A special case may be cited to illustrate the principle of applying this process, the sugars present, for example, being raffinose, cane sugar, and monoses; the ferments used were *S. cerevisiæ* (under-yeast U), ordinary press yeast, *Torula dattila* and *Torula monosa*. The difference between the results with the first two yeasts gives the raffinose; the cane sugar can then be calculated from the volume of gas given by *Torula dattila*, after allowing for the raffinose present, whilst the gas evolved by *Torula monosa* is a measure of the hexoses present (dextrose, lævulose or mannose), as only these sugars are fermented by this organism. The process is said to be relatively rapid and to give approximately accurate results in cases where other methods are inapplicable. Biochemical methods have been applied

<sup>1</sup> *Ann. Inst. Pasteur*, 1906, 20, 977.

by Kluyver to the analysis of food materials such as jams, potato syrups and to other cases of technical importance.

The experiments of Bertrand and Weisweiler<sup>1</sup> and Bertrand and Ducháček<sup>1</sup> have shown that the Bulgarian bacillus (*Bacillus acidi lactici Massol*) is capable of converting hexoses such as *d*-glucose, lævulose, mannose and galactose into lactic acid, but acts upon only one of the disaccharides in this way, namely, lactose. Saccharose and maltose are not attacked by this organism, and Margailan suggested that the latter should be used as a means of separating cane sugar from lactose and *d*-glucose. Testoni<sup>2</sup> has worked out a process of estimating saccharose in condensed milk and similar materials based on this principle. 20 gm. of condensed milk are dissolved in warm water and mixed with acetic acid to coagulate proteins, and then with basic lead acetate, the excess of lead being removed by means of a saturated solution of sodium sulphate. The solution is made up to 200 c.c., and an additional 2 c.c. of water are added to compensate for the volume of the coagulum. 100 c.c. of the filtrate are mixed with malt-peptone and 3 gm. of powdered marble, neutralised exactly, using phenolphthaleïn as indicator, and sterilised. The solution is inoculated with a pure culture of the bacillus and left for 6 days in an incubator at 35°. The lactic acid formed is precipitated by adding a slight excess of zinc sulphate and the volume made up to 100 c.c.; the solution is quickly filtered and the rotatory power measured with the polarimeter.

Jolles<sup>3</sup> has stated that arabinose, rhamnose, *d*-glucose, fructose, galactose, mannose, invert sugar, maltose and lactose are completely decomposed when heated with *N*/10 sodium hydroxide during 45 minutes in the water-bath or during 24 hours in a thermostat at 37°, acid substances being formed which are without action on polarised light; saccharose, on the other hand, is not in the least affected by this treatment, so that it is possible to estimate this substance in presence of the above-named sugars by treatment with sodium hydroxide under the conditions named. Testoni states that Jolles' method gives the same results with sweetened wines, condensed milk and marmalades as are obtained by his process of fermentation<sup>4</sup> and as the treatment with sodium hydroxide can be carried out rapidly, Jolles' method is preferable in most cases to the more tedious fermentation process. It is best to work at 37° rather than 100° as at the lower temperature darkening of the solution and the consequent difficulty of reading the rotatory power of the solution are avoided. Before measuring the rotation the solution should be neutralised or made slightly acid with acetic acid, as otherwise the readings are slightly low. The nature of the change of rotation brought about by treatment with sodium hydroxide indicates whether commercial glucose or invert sugar was originally present. Bardach and Silberstein<sup>5</sup> have also applied Jolles' process to a number of commercial preparations.

<sup>1</sup> *Ann. Inst. Pasteur*, 1909, 23, 402.

<sup>2</sup> *Ann. Lab. Centr. delle Gabelle*, 1912, page 581.

<sup>3</sup> *Zeit. Nahr. und Genussm.*, 1910, 20, 631.

<sup>4</sup> Compare Nowak, *Zeit. Anal. Chem.*, 1912, 51, 610.

<sup>5</sup> *Zeit. Nahr. und Genussm.*, 1911, 21, 540.

**Lactose.**

Cole<sup>1</sup> has given the following table for lactose. He makes use of the iodometric method in estimating the copper, under the following conditions: Into a 200 c.c. Erlenmeyer flask measure 20 c.c. of standardised copper sulphate, 20 c.c. of the alkaline copper tartrate and 20 c.c. of the sugar solution to be tested (which must contain between 5 and 250 mm. of anhydrous lactose). Fit a two-holed rubber stopper firmly into the neck of the flask, adjust a thermometer so that its lower end is 2 mm. from the bottom of the flask and place the latter on the heated gauze. Note the time when the mercury indicates a temperature of 95° and allow the heating to continue for exactly 20 seconds beyond this. Remove the flask by gripping the rubber stopper and rapidly cool under the tap. Filter the hot solution at once, using the stem of the thermometer as a stirring rod. Wash the flask twice with about 7 c.c. of distilled water, cool the filtrate under the tap, add exactly 4 c.c. of concentrated sulphuric acid, insert a thermometer and cool to 20°. Add 6.5 to 7 c.c. of a saturated solution of potassium iodide, washing the stem of the thermometer with this solution. Titrate at once with the standardised solution of sodium thiosulphate in the usual way, using soluble starch as indicator.<sup>2</sup>

TABLE VIII.—REDUCING POWER OF LACTOSE (Cole.)

Anhydrous lactose	Copper mg.	Lactose: copper
5	4.4	1.136
10	9.8	1.020
15	16.6	0.903
20	24.1	0.830
25	30.5	0.820
30	36.9	0.813
35	43.2	0.810
40	49.9	0.802
45	56.1	0.802
50	62.5	0.800
55	69.0	0.805
60	75.2	0.798
65	81.3	0.799
70	88.2	0.793
75	94.0	0.798
80	100.9	0.793
85	107.3	0.792
90	113.6	0.792
95	120.1	0.791
100	127.0	0.788
120	152.8	0.786
130	166.1	0.783
140	179.4	0.780
150	191.6	0.783
175	223.0	0.785
200	255.5	0.782
240	307.3	0.781
250	320.7	0.780

Below are given the values for lactose which are employed provisionally in the United States by the A. O. A. C.; they were obtained by the gravimetric method described on page 28, and supplement the tables given on pages 29 to 37 for other sugars.

<sup>1</sup> *Biochem. J.*, 1914, 8, 134.

<sup>2</sup> Cole attributes the method of estimating sugars iodometrically to Peters (*J. Amer. Chem. Soc.*, 1912, 34, 422 and 928). Schoorl in 1899 suggested substantially the same process (see page 41) and gave tables of reducing values.

TABLE IX.—TABLE FOR CALCULATING LACTOSE.

(Correction for *Bulletin* 107 (*revised*), pages 243-251.)

(From *Circular* 82, U. S. Dept. of Agric., Dec. 30, 1911.)

(Expressed in milligrams.)

Cu- prous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Lactose			Cu- prous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Lactose		
		(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> )	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ½H <sub>2</sub> O)	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ,H <sub>2</sub> O)			(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> )	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ½H <sub>2</sub> O)	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ,H <sub>2</sub> O)
10	8.9	3.8	3.9	4.0	65	57.7	40.0	41.0	42.1
11	9.8	4.5	4.6	4.7	66	58.6	40.6	41.7	42.8
12	10.7	5.1	5.3	5.4	67	59.5	41.3	42.4	43.5
13	11.5	5.8	5.9	6.1	68	60.4	41.9	43.1	44.2
14	12.4	6.4	6.6	6.8	69	61.3	42.6	43.7	44.8
15	13.3	7.1	7.3	7.5	70	62.2	43.3	44.4	45.5
16	14.2	7.8	8.0	8.2	71	63.1	43.9	45.1	46.2
17	15.1	8.4	8.6	8.9	72	64.0	44.6	45.8	46.9
18	16.0	9.1	9.3	9.5	73	64.8	45.2	46.4	47.6
19	16.9	9.7	10.0	10.2	74	65.7	45.9	47.1	48.3
20	17.8	10.4	10.7	10.9	75	66.6	46.6	47.8	49.0
21	18.7	11.0	11.3	11.6	76	67.5	47.2	48.5	49.7
22	19.5	11.7	12.0	12.3	77	68.4	47.9	49.1	50.4
23	20.4	12.3	12.7	13.0	78	69.3	48.5	49.8	51.1
24	21.3	13.0	13.4	13.7	79	70.2	49.2	50.5	51.8
25	22.2	13.7	14.0	14.4	80	71.1	49.9	51.2	52.5
26	23.1	14.3	14.7	15.1	81	71.9	50.5	51.9	53.2
27	24.0	15.0	15.4	15.8	82	72.8	51.2	52.5	53.9
28	24.9	15.6	16.1	16.5	83	73.7	51.8	53.2	54.6
29	25.8	16.3	16.7	17.1	84	74.6	52.5	53.9	55.3
30	26.6	16.9	17.4	17.8	85	75.5	53.1	54.6	56.0
31	27.5	17.6	18.1	18.5	86	76.4	53.8	55.2	56.6
32	28.4	18.3	18.7	19.2	87	77.3	54.5	55.9	57.3
33	29.3	18.9	19.4	19.9	88	78.2	55.1	56.6	58.0
34	30.2	19.6	20.1	20.6	89	79.1	55.8	57.3	58.7
35	31.1	20.2	20.8	21.3	90	79.9	56.4	58.0	59.4
36	32.0	20.9	21.4	22.0	91	80.8	57.1	58.6	60.1
37	32.9	21.5	22.1	22.7	92	81.7	57.8	59.3	60.8
38	33.8	22.2	22.8	23.4	93	82.6	58.4	60.0	61.5
39	34.6	22.8	23.5	24.1	94	83.5	59.1	60.7	62.2
40	35.5	23.5	24.1	24.8	95	84.4	59.7	61.3	62.9
41	36.4	24.2	24.8	25.4	96	85.3	60.4	62.0	63.6
42	37.3	24.8	25.5	26.1	97	86.2	61.1	62.7	64.3
43	38.2	25.5	26.2	26.8	98	87.0	61.7	63.4	65.0
44	39.1	26.1	26.8	27.5	99	87.9	62.4	64.0	65.7
45	40.0	26.8	27.5	28.2	100	88.8	63.0	64.7	66.4
46	40.9	27.4	28.2	28.9	101	89.7	63.7	65.4	67.1
47	41.7	28.1	28.9	29.6	102	90.6	64.4	66.1	67.8
48	42.6	28.7	29.5	30.3	103	91.5	65.0	66.7	68.5
49	43.5	29.4	30.2	31.0	104	92.4	65.7	67.4	69.1
50	44.4	30.1	30.9	31.7	105	93.3	66.4	68.1	69.8
51	45.3	30.7	31.5	32.4	106	94.2	67.0	68.8	70.5
52	46.2	31.4	32.2	33.0	107	95.0	67.7	69.5	71.2
53	47.1	32.1	32.9	33.7	108	95.9	68.3	70.1	71.9
54	48.0	32.7	33.6	34.4	109	96.8	69.0	70.8	72.6
55	48.9	33.4	34.3	35.1	110	97.7	69.7	71.5	73.3
56	49.7	34.0	34.9	35.8	111	98.6	70.3	72.2	74.0
57	50.6	34.7	35.6	36.5	112	99.5	71.0	72.8	74.7
58	51.5	35.4	36.3	37.2	113	100.4	71.6	73.5	75.4
59	52.4	36.0	37.0	37.9	114	101.3	72.3	74.2	76.1
60	53.3	36.7	37.6	38.6	115	102.1	73.0	74.9	76.8
61	54.2	37.3	38.3	39.3	116	103.0	73.6	75.6	77.5
62	55.1	38.0	39.0	40.0	117	103.9	74.3	76.2	78.2
63	56.0	38.6	39.7	40.7	118	104.8	75.0	76.9	78.9
64	56.8	39.3	40.3	41.4	119	105.7	75.6	77.6	79.6

TABLE IX.—TABLE FOR CALCULATING LACTOSE.—*Continued.*

Cu- prous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Lactose			Cu- prous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Lactose		
		(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> )	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ½H <sub>2</sub> O	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ,H <sub>2</sub> O)			(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> )	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ½H <sub>2</sub> O	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ,H <sub>2</sub> O)
120	106.6	76.3	78.3	80.3	180	159.9	116.1	119.1	122.2
121	107.5	76.9	79.0	81.0	181	160.8	116.7	119.8	122.9
122	108.4	77.6	79.6	81.7	182	161.7	117.4	120.5	123.6
123	109.3	78.3	80.3	82.4	183	162.5	118.1	121.2	124.3
124	110.1	78.9	81.0	83.1	184	163.4	118.7	121.8	125.0
125	111.0	79.6	81.7	83.8	185	164.3	119.4	122.5	125.7
126	111.9	80.3	82.4	84.5	186	165.2	120.1	123.2	126.4
127	112.8	80.9	83.0	85.2	187	166.1	120.7	123.9	127.1
128	113.7	81.6	83.7	85.9	188	167.0	121.4	124.6	127.8
129	114.6	82.2	84.4	86.6	189	167.9	122.1	125.3	128.5
130	115.5	82.9	85.1	87.3	190	168.8	122.7	125.9	129.2
131	116.4	83.6	85.7	88.0	191	169.7	123.4	126.6	129.9
132	117.2	84.2	86.4	88.7	192	170.5	124.1	127.3	130.6
133	118.1	84.9	87.1	89.4	193	171.4	124.7	128.0	131.3
134	119.0	85.5	87.8	90.1	194	172.3	125.4	128.7	132.0
135	119.9	86.2	88.5	90.8	195	173.2	126.1	129.4	132.7
136	120.8	86.9	89.1	91.5	196	174.1	126.7	130.0	133.4
137	121.7	87.5	89.8	92.1	197	175.0	127.4	130.7	134.1
138	122.6	88.2	90.5	92.8	198	175.9	128.1	131.4	134.8
139	123.5	88.9	91.2	93.5	199	176.8	128.7	132.1	135.5
140	124.4	89.5	91.9	94.2	200	177.6	129.4	132.8	136.2
141	125.2	90.2	92.5	94.9	201	178.5	130.0	133.5	136.9
142	126.1	90.8	93.2	95.6	202	179.4	130.7	134.1	137.6
143	127.0	91.5	93.9	96.3	203	180.3	131.4	134.8	138.3
144	127.9	92.2	94.6	97.0	204	181.2	132.0	135.5	139.0
145	128.8	92.8	95.3	97.7	205	182.1	132.7	136.2	139.7
146	129.7	93.5	95.9	98.4	206	183.0	133.4	136.9	140.4
147	130.6	94.2	96.6	99.1	207	183.9	134.0	137.6	141.1
148	131.5	94.8	97.3	99.8	208	184.8	134.7	138.3	141.8
149	132.3	95.5	98.0	100.5	209	185.6	135.4	138.9	142.5
150	133.2	96.1	98.7	101.2	210	186.5	136.0	139.6	143.2
151	134.1	96.8	99.3	101.9	211	187.4	136.7	140.3	143.9
152	135.0	97.5	100.0	102.6	212	188.3	137.4	141.0	144.6
153	135.9	98.1	100.7	103.3	213	189.2	138.0	141.7	145.3
154	136.8	98.8	101.4	104.0	214	190.1	138.7	142.4	146.0
155	137.7	99.5	102.1	104.7	215	191.0	139.4	143.0	146.7
156	138.6	100.1	102.8	105.4	216	191.9	140.0	143.7	147.4
157	139.5	100.8	103.4	106.1	217	192.7	140.7	144.4	148.1
158	140.3	101.5	104.1	106.8	218	193.6	141.4	145.1	148.8
159	141.2	102.1	104.8	107.5	219	194.5	142.0	145.8	149.5
160	142.1	102.8	105.5	108.2	220	195.4	142.7	146.5	150.2
161	143.0	103.4	106.2	108.9	221	196.3	143.4	147.2	150.9
162	143.9	104.1	106.8	109.6	222	197.2	144.0	147.8	151.6
163	144.8	104.8	107.5	110.3	223	198.1	144.7	148.5	152.3
164	145.7	105.4	108.2	111.0	224	199.0	145.4	149.2	153.0
165	146.6	106.1	108.9	111.7	225	199.8	146.0	149.9	153.7
166	147.4	106.8	109.6	112.4	226	200.7	146.7	150.6	154.4
167	148.3	107.4	110.3	113.1	227	201.6	147.4	151.3	155.1
168	149.2	108.1	110.9	113.8	228	202.5	148.0	152.0	155.8
169	150.1	108.8	111.6	114.5	229	203.4	148.7	152.6	156.5
170	151.0	109.4	112.3	115.2	230	204.3	149.4	153.3	157.2
171	151.9	110.1	113.0	115.9	231	205.2	150.0	154.0	157.9
172	152.8	110.8	113.7	116.6	232	206.1	150.7	154.7	158.6
173	153.7	111.4	114.3	117.3	233	207.0	151.4	155.4	159.3
174	154.6	112.1	115.0	118.0	234	207.8	152.0	156.1	160.0
175	155.4	112.8	115.7	118.7	235	208.7	152.7	156.7	160.7
176	156.3	113.4	116.4	119.4	236	209.6	153.4	157.4	161.4
177	157.2	114.1	117.1	120.1	237	210.5	154.0	158.1	162.1
178	158.1	114.8	117.8	120.8	238	211.4	154.7	158.8	162.8
179	159.0	115.4	118.4	121.5	239	212.3	155.4	159.5	163.5



TABLE IX.—TABLE FOR CALCULATING LACTOSE.—Continued.

Cu- prous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Lactose			Cu- prous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Lactose		
		(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> )	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ½H <sub>2</sub> O)	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> , H <sub>2</sub> O)			(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> )	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ½H <sub>2</sub> O)	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> , H <sub>2</sub> O)
240	213.2	156.1	160.2	164.3	305	270.9	199.6	204.9	210.1
241	214.1	156.7	160.9	165.0	306	271.8	200.3	205.5	210.8
242	214.9	157.4	161.5	165.7	307	272.7	201.0	206.2	211.5
243	215.8	158.1	162.2	166.4	308	273.6	201.6	206.9	212.2
244	216.7	158.7	162.9	167.1	309	274.5	202.3	207.6	212.9
245	217.6	159.4	163.6	167.8	310	275.3	203.0	208.3	213.7
246	218.5	160.1	164.3	168.5	311	276.2	203.6	209.0	214.4
247	219.4	160.7	165.0	169.2	312	277.1	204.3	209.7	215.1
248	220.3	161.4	165.7	169.9	313	278.0	205.0	210.4	215.8
249	221.2	162.1	166.3	170.6	314	278.9	205.7	211.1	216.5
250	222.1	162.7	167.0	171.3	315	279.8	206.3	211.8	217.2
251	222.9	163.4	167.7	172.0	316	280.7	207.0	212.5	217.9
252	223.8	164.1	168.4	172.7	317	281.6	207.7	213.1	218.6
253	224.7	164.7	169.1	173.4	318	282.5	208.4	213.8	219.3
254	225.6	165.4	169.8	174.1	319	283.3	209.0	214.5	220.0
255	226.5	166.1	170.5	174.8	320	284.2	209.7	215.2	220.7
256	227.4	166.8	171.1	175.5	321	285.1	210.4	215.9	221.4
257	228.3	167.4	171.8	176.2	322	286.0	211.0	216.6	222.2
258	229.2	168.1	172.5	176.9	323	286.9	211.7	217.3	222.9
259	230.0	168.8	173.2	177.6	324	287.8	212.4	218.0	223.6
260	230.9	169.4	173.9	178.3	325	288.7	213.1	218.7	224.3
261	231.8	170.1	174.6	179.0	326	289.6	213.7	219.4	225.0
262	232.7	170.8	175.3	179.8	327	290.4	214.4	220.1	225.7
263	233.6	171.4	176.0	180.5	328	291.3	215.1	220.7	226.4
264	234.5	172.1	176.6	181.2	329	292.2	215.8	221.4	227.1
265	235.4	172.8	177.3	181.9	330	293.1	216.4	222.1	227.8
266	236.3	173.5	178.0	182.6	331	294.0	217.1	222.8	228.5
267	237.2	174.1	178.7	183.3	332	294.9	217.8	223.5	229.2
268	238.0	174.8	179.4	184.0	333	295.8	218.4	224.2	230.0
269	238.9	175.5	180.1	184.7	334	296.7	219.1	224.9	230.7
270	239.8	176.1	180.8	185.4	335	297.6	219.8	225.6	231.4
271	240.7	176.8	181.5	186.1	336	298.4	220.5	226.3	232.1
272	241.6	177.5	182.1	186.8	337	299.3	221.1	227.0	232.8
273	242.5	178.1	182.8	187.5	338	300.2	221.8	227.7	233.5
274	243.4	178.8	183.5	188.2	339	301.1	222.5	228.3	234.2
275	244.3	179.5	184.2	188.9	340	302.0	223.2	229.0	234.9
276	245.1	180.2	184.9	189.6	341	302.9	223.8	229.7	235.6
277	246.0	180.8	185.6	190.3	342	303.8	224.5	230.4	236.3
278	246.9	181.5	186.3	191.0	343	304.7	225.2	231.1	237.0
279	247.8	182.2	187.0	191.7	344	305.5	225.9	231.8	237.8
280	248.7	182.8	187.7	192.4	345	306.4	226.5	232.5	238.5
281	249.6	183.5	188.3	193.1	346	307.3	227.2	233.2	239.2
282	250.5	184.2	189.0	193.9	347	308.2	227.9	233.9	239.9
283	251.4	184.8	189.7	194.6	348	309.1	228.5	234.6	240.6
284	252.3	185.5	190.4	195.3	349	310.0	229.2	235.3	241.3
285	253.1	186.2	191.1	196.0	350	310.9	229.9	235.9	242.0
286	254.0	186.9	191.8	196.7	351	311.8	230.6	236.6	242.7
287	254.9	187.5	192.5	197.4	352	312.7	231.2	237.3	243.4
288	255.8	188.2	193.2	198.1	353	313.5	231.9	238.0	244.1
289	256.7	188.9	193.8	198.8	354	314.4	232.6	238.7	244.8
290	257.6	189.5	194.5	199.5	355	315.3	233.3	239.4	245.6
291	258.5	190.2	195.2	200.2	356	316.2	233.9	240.1	246.3
292	259.4	190.9	195.9	200.9	357	317.1	234.6	240.8	247.0
293	260.2	191.5	196.6	201.6	358	318.0	235.3	241.5	247.7
294	261.1	192.2	197.3	202.3	359	318.9	236.0	242.2	248.4
295	262.0	192.9	198.0	203.0	360	319.8	236.7	242.9	249.1
296	262.9	193.6	198.7	203.7	361	320.6	237.3	243.6	249.8
297	263.8	194.2	199.3	204.4	362	321.5	238.0	244.3	250.5
298	264.7	194.9	200.0	205.1	363	322.4	238.7	245.0	251.2
299	265.6	195.6	200.7	205.8	364	323.3	239.4	245.7	252.0
300	266.5	196.2	201.4	206.6	365	324.2	240.0	246.4	252.7
301	267.4	196.9	202.1	207.3	366	325.1	240.7	247.0	253.4
302	268.2	197.6	202.8	208.0	367	326.0	241.4	247.7	254.1
303	269.1	198.3	203.5	208.7	368	326.9	242.1	248.4	254.8
304	270.0	198.9	204.2	209.4	369	327.8	242.7	249.1	255.5

TABLE IX.—TABLE FOR CALCULATING LACTOSE.—*Continued.*

Cu- prous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Lactose			Cu- prous oxide (Cu <sub>2</sub> O)	Copper (Cu)	Lactose		
		(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> )	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ½H <sub>2</sub> O)	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> , H <sub>2</sub> O)			(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> )	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ½H <sub>2</sub> O)	(C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> , H <sub>2</sub> O)
370	328.6	243.4	249.8	256.2	430	381.9	284.1	291.5	299.0
371	329.5	244.1	250.5	256.9	431	382.8	284.7	292.2	299.7
372	330.4	244.8	251.2	257.7	432	383.7	285.4	292.9	300.5
373	331.3	245.4	251.9	258.4	433	384.6	286.1	293.6	301.2
374	332.2	246.1	252.6	259.1	434	385.5	286.8	294.3	301.9
375	333.1	246.8	253.3	259.8	435	386.4	287.5	295.0	302.6
376	334.0	247.5	254.0	260.5	436	387.3	288.1	295.7	303.3
377	334.9	248.1	254.7	261.2	437	388.2	288.8	296.4	304.0
378	335.7	248.8	255.4	261.9	438	389.0	289.5	297.1	304.7
379	336.6	249.5	256.1	262.6	439	389.9	290.2	297.8	305.5
380	337.5	250.2	256.8	263.4	440	390.8	290.9	298.5	306.2
381	338.4	250.8	257.5	264.1	441	391.7	291.5	299.2	306.9
382	339.3	251.5	258.1	264.8	442	392.6	292.2	299.9	307.6
383	340.2	252.2	258.8	265.5	443	393.5	292.9	300.6	308.3
384	341.1	252.9	259.5	266.2	444	394.4	293.6	301.3	309.0
385	342.0	253.6	260.2	266.9	445	395.3	294.2	302.0	309.7
386	342.9	254.2	260.9	267.6	446	396.1	294.9	302.7	310.5
387	343.7	254.9	261.6	268.3	447	397.0	295.6	303.4	311.2
388	344.6	255.6	262.3	269.0	448	397.9	296.3	304.1	311.9
389	345.5	256.3	263.0	269.8	449	398.8	297.0	304.8	312.6
390	346.4	256.9	263.7	270.5	450	399.7	297.6	305.5	313.3
391	347.3	257.6	264.4	271.2	451	400.6	298.3	306.2	314.0
392	348.2	258.3	265.1	271.9	452	401.5	299.0	306.9	314.7
393	349.1	259.0	265.8	272.6	453	402.4	299.7	307.6	315.5
394	350.0	259.6	266.5	273.3	454	403.3	300.4	308.3	316.2
395	350.8	260.3	267.2	274.0	455	404.1	301.1	309.0	316.9
396	351.7	261.0	267.9	274.7	456	405.0	301.7	309.7	317.6
397	352.6	261.7	268.6	275.5	457	405.9	302.4	310.4	318.3
398	353.5	262.3	269.3	276.2	458	406.8	303.1	311.1	319.0
399	354.4	263.0	269.9	276.9	459	407.7	303.8	311.8	319.8
400	355.3	263.7	270.6	277.6	460	408.6	304.5	312.5	320.5
401	356.2	264.4	271.3	278.3	461	409.5	305.1	313.2	321.2
402	357.1	265.0	272.0	279.0	462	410.4	305.8	313.9	321.9
403	358.0	265.7	272.7	279.7	463	411.2	306.5	314.6	322.6
404	358.8	266.4	273.4	280.4	464	412.1	307.2	315.3	323.4
405	359.7	267.1	274.1	281.1	465	413.0	307.9	316.0	324.1
406	360.6	267.8	274.8	281.9	466	413.9	308.6	316.7	324.8
407	361.5	268.4	275.5	282.6	467	414.8	309.2	317.4	325.5
408	362.4	269.1	276.2	283.3	468	415.7	309.9	318.1	326.2
409	363.3	269.8	276.9	284.0	469	416.6	310.6	318.8	326.9
410	364.2	270.5	277.6	284.7	470	417.5	311.3	319.5	327.7
411	365.1	271.2	278.3	285.4	471	418.4	312.0	320.2	328.4
412	365.9	271.8	279.0	286.2	472	419.2	312.6	320.9	329.1
413	366.8	272.5	279.7	286.9	473	420.1	313.3	321.6	329.8
414	367.7	273.2	280.4	287.6	474	421.0	314.0	322.3	330.5
415	368.6	273.9	281.1	288.3	475	421.9	314.7	323.0	331.3
416	369.5	274.6	281.8	289.0	476	422.8	315.4	323.7	332.0
417	370.4	275.2	282.5	289.7	477	423.7	316.1	324.4	332.7
418	371.3	275.9	283.2	290.4	478	424.6	316.7	325.1	333.4
419	372.2	276.6	283.9	291.2	479	425.5	317.4	325.8	334.1
420	373.1	277.3	284.6	291.9	480	426.3	318.1	326.5	334.8
421	373.9	277.9	285.3	292.6	481	427.2	318.8	327.2	335.6
422	374.8	278.6	286.0	293.3	482	428.1	319.5	327.9	336.3
423	375.7	279.3	286.7	294.0	483	429.0	320.1	328.6	337.0
424	376.6	280.0	287.4	294.7	484	429.9	320.8	329.3	337.7
					485	430.8	321.5	330.0	338.4
425	377.5	280.7	288.1	295.4	486	431.7	322.2	330.7	339.1
426	378.4	281.3	288.8	296.2	487	432.6	322.9	331.4	339.9
427	379.3	282.0	289.4	296.9	488	433.5	323.6	332.1	340.6
428	380.2	282.7	290.1	297.6	489	434.3	324.2	332.8	341.3
429	381.0	283.4	290.8	298.3	490	435.2	324.9	333.5	342.0



The method which is provisional in the United States<sup>1</sup> of estimating lactose and succharose in presence of one another, for example in cocoa products, is given in full in Vol. 6, page 713 (Dubois' method). As this method is purely a polarimetric one and the presence of salts and other substances in special cases may falsify the results by modifying the optical data, it is always advisable to check the results obtained by an alternative process. The lactose itself, for example, can be estimated in presence of saccharose by measuring its reducing power; this can be done either volumetrically or gravimetrically. If the volumetric process be adopted the Fehling solution should be standardised against pure lactose; and if the gravimetric method be followed tables should be used or prepared for the precise conditions under which the estimation is carried out. The cane sugar can be estimated separately by measuring the change of reducing and specific rotatory powers brought about by invertase (autolysed yeast, see page 46). In presence of fermentable sugars such as maltose, invert sugar, cane sugar, etc., lactose can be estimated by fermenting away these sugars by means of ordinary yeast and then measuring the reducing power or rotatory power of the residual material; lactose is not fermented by ordinary yeast.

### Pentoses and Pentosans.

The reducing powers of pure arabinose and xylose under the standard conditions of Brown, Morris and Millar (page 24) have been determined by Daish.<sup>2</sup> The values obtained are given in Tables X and XI below, and refer to the anhydrous sugars.

TABLE X.—REDUCING POWER OF ARABINOSE.

$$[\alpha]_D^{20} = 102.2^\circ \text{ (c = 6.80).}$$

Milligrams, arabinose	Grams, CuO	Calculated divisor	Divisor from curve
10	0.0270	2.700	2.669
20	0.0540	2.700	2.654
30	0.0804	2.680	2.640
40	0.1064	2.660	2.625
50	0.1320	2.640	2.610
60	0.1570	2.617	2.595
70	0.1820	2.600	2.581
80	0.2060	2.575	2.566
90	0.2300	2.556	2.551
100	0.2540	2.540	2.536
110	0.2780	2.527	2.521
120	0.3020	2.517	2.507
130	0.3248	2.499	2.492
140	0.3476	2.483	2.477
150	0.3700	2.467	2.461
160	0.3920	2.450	2.447
170	0.4140	2.435	2.432
180	0.4360	2.422	2.417
190	0.4570	2.405	2.403
200	0.4780	2.390	2.381

<sup>1</sup> *Bulletin* 107 (revised), 1912, p. 256.

<sup>2</sup> *J. Agric. Sci.*, 1914, 6, 225.

TABLE XI.—REDUCING POWER OF XYLOSE.

$$[\alpha]_D^{20} = 18.78^\circ (c = 5.07)$$

Milligrams, xylose	Grams, CuO	Calculated divisor	Divisor from curve
10	0.0280	2.800	2.656
20	0.0540	2.700	2.638
30	0.0798	2.660	2.620
40	0.1040	2.600	2.602
50	0.1300	2.600	2.581
60	0.1540	2.583	2.563
70	0.1790	2.557	2.545
80	0.2030	2.537	2.526
90	0.2260	2.511	2.508
100	0.2490	2.490	2.490
110	0.2720	2.473	2.471
120	0.2940	2.450	2.453
130	0.3160	2.431	2.433
140	0.3380	2.414	2.415
150	0.3600	2.400	2.397
160	0.3810	2.381	2.378
170	0.4020	2.365	2.360
180	0.4230	2.350	2.341
190	0.4440	2.337	2.322
200	0.4640	2.320	2.304

It will be seen that the reducing powers of xylose and arabinose are almost identical. For practical purposes when working with the unknown pentoses in plant extracts it is probable that no large error will be incurred by taking as the divisor the average value for arabinose and xylose corresponding with the weight of CuO dealt with. The reducing powers of arabinose and xylose differ too only slightly from that of dextrose; thus the divisors for these three sugars for 100 mg. of sugar, are respectively 2.536, 2.490 and 2.538.

Pentoses are generally present in appreciable quantity in the solutions obtained by extracting foliage leaves with alcohol; when such solutions have been treated with basic lead acetate in the usual way and the excess of lead has been removed by means of sodium carbonate, or other precipitant, these pentoses exercise a reducing action on Fehling's solution. When, therefore, it is necessary to make an analysis of such material, allowance must be made for these sugars, as indicated in the scheme given on page 64, before it is possible to calculate the proportion of other reducing sugar present, such as dextrose and lævulose.<sup>1</sup>

Kluyver (*Biochemische Suikerbepalingen*, 1914, page 181), considered that pentoses in the free state do not usually occur in plant extracts but Davis and Sawyer<sup>2</sup> have since given definite proof of their presence in extracts of certain leaves (turnip, mangold). Kluyver emphasised the fact that when other sugars, such as cane sugar, lævulose, etc., are present, the values obtained by the ordinary Tollens-Kröber method of estimating pentoses by distillation with hydrochloric acid are high owing to the formation of a furfural-like substance (probably hydroxymethylfurfuraldehyde) which yields an insoluble phloroglucide; the presence of pentoses might therefore

<sup>1</sup> Davis and Daish, *J. Agric. Sci.*, 1914, 5, 465.

<sup>2</sup> *J. Agric. Sci.*, 1914, 6, 406.

be inferred in cases when these sugars were really absent, owing to the action of the hydrochloric acid used on sugars such as saccharose, dextrose and lævulose which were present in relative excess. Kluyver also suggested that the pentose estimation should only be carried out after fermenting away the other sugars. Davis and Sawyer, however, show (*loc. cit.*) that the error caused by the presence of these in estimating the pentoses in plant extracts is relatively small and for most practical purposes can be neglected.

Cunningham and Dorée<sup>1</sup> have discussed at some length the formation of hydroxyfurfuraldehyde from various carbohydrates. They show that the condensation which produces furfural in the case of pentoses or pentosans takes place rapidly and is almost completed before the hydroxymethyl-derivative begins to distil over. By using aniline acetate test paper it is possible to distinguish between the separation of the two aldehydes and practically no error is made in pentosan estimations if this indicator is used. The hydroxyaldehyde is produced at a very slow rate. Its total amount is small, varying between 1 and 2% in the case of the hexoses and those celluloses which contain little or no pentosan. The probable reason for this is the ready hydrolysis of the hydroxymethylfurfuraldehyde to formic and lævulic acids. This property explains the well-known observations of Fraps<sup>2</sup> who found that when the distillates obtained from a number of natural products, food stuffs, etc., were distilled again, a considerable loss of "furfural" occurred. With pure furfuraldehyde this did not occur. He considered that the portion which disappeared could not be regarded as due to true pentosan and in the absence of further knowledge designated it as the "furaloid" constituent. In all probability the "furaloid" is a hexose-yielding constituent which gives hydroxymethylaldehyde and this on a second distillation is largely decomposed.

The formation of the hydroxymethylaldehyde under the conditions given above, makes estimations of methylpentosans, by the method of Ellet and Tollens<sup>3</sup> of doubtful value.

**Estimation of Carbohydrates in Plant Extracts.**—The following scheme for the analysis of plant material such as foliage leaves, seeds, etc., has been suggested by Davis and Daish.<sup>4</sup>

The material immediately, after picking, is dropped into a large volume (2 litres) of boiling alcohol to which a little ammonia has been added (10 to 20 c.c. of ammonia, sp. gr. 0.880). This treatment destroys all the enzymes which are present and prevents change of the sugars during subsequent treatment.

The plant material is extracted in a large metal Soxhlet extractor for 18 hours. The extract is then evaporated *in vacuo* (60 to 20 mm.) to a small bulk and made up to a definite volume, *e.g.*, 500 c.c. Of this, two portions

<sup>1</sup> *Biochem. J.*, 1914, 8, 438.

<sup>2</sup> *Amer. Chem. J.*, 1901, 25, 201.

<sup>3</sup> *J. Landwirth.*, 1905, 53, 13.

<sup>4</sup> *J. Agric. Sci.*, 1913, 5, 437.

of 20 c.c. each are evaporated to dryness and dried *in vacuo* for 18 hours at 100° C. This gives the total dry matter in the extract. 440 c.c. are treated with the requisite volume of basic lead acetate solution, filtered under pressure on a Buchner funnel, washed and made up to a known volume, 2 litres. This is called Solution A.<sup>1</sup>

300 c.c. of Solution A are delead by means of solid Na<sub>2</sub>CO<sub>3</sub>, avoiding much excess, and made up to 500 c.c. This is called Solution B.

(1) 25 c.c. of B are used for the *direct reduction* and *polarisation*;<sup>2</sup> the reduction is due to dextrose, lævulose, maltose, pentoses.

(2) **For Saccharose.**—Invert 50 c.c. of B:

(a) By invertase. Make neutral to methyl-orange by a few drops of concentrated sulphuric acid, and add 1–2 c.c. of autolysed yeast and 2 or 3 drops of toluene and leave 24 hours at 38–40° C. After this period, add 5 to 10 c.c. alumina cream, filter and wash to 100 c.c. Take the reducing power of 50 c.c. (= 25 c.c. B) and polarise.

(b) By 10% citric acid. Make faintly acid to methyl-orange by adding a few drops of concentrated sulphuric acid and add a weighed quantity of citric acid crystals so as to have 10% of the crystalline acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> + H<sub>2</sub>O) present. Boil 10 minutes, cool, neutralise (to phenolphthaleïn) with sodium hydroxide, make to 100 c.c. and determine the reducing power of 50 c.c. (= 25 c.c. B); polarise in faintly acid solution.

**Saccharose** is calculated from the increase of reducing power or change of rotation caused by inversion. The values obtained by the two methods (a) and (b) should agree closely.

(3) **For Maltose.**—Another 300 c.c. of Solution A is delead by means of hydrogen sulphide and filtered, the precipitated sulphide being washed until the total volume of filtrate and washings is about 450 c.c. Air is then sucked through this for about 1½ hours to expel hydrogen sulphide, a very little ferric hydroxide is added to remove the last traces of the latter, and the solution is made to 500 c.c. It is filtered and

50 c.c. fermented (a) with *S. marxianus*  
 50 c.c. fermented (b) with *S. anomalus*  
 50 c.c. fermented (c) with *S. exiguus*

and two lots *d* and *e* of 50 c.c. are fermented with baker's yeast. It is generally necessary in order to ensure good growth of the yeast to reduce the acidity by adding 2 to 5 c.c. of *N*-sodium carbonate to the 50 c.c. to be fermented; 5 c.c. of sterilised yeast water is also added, the mixture is sterilised in the usual way and inoculated in the inoculating chamber with the pure culture

<sup>1</sup> It is often preferable when the solutions contain relatively small quantities of sugars to add sodium carbonate (or sodium sulphate) to remove the excess of lead before completing the volume to 2 litres. In such cases solution A, after filtering, is used directly for the sugar estimations.

<sup>2</sup> The polarisation of these dilute solutions is usually small and it is therefore necessary to take the reading in a long tube (at least 200 mm. in length) with an instrument reading accurately to 1/100°, the temperature being maintained constant at 20° C. within 1/10°. It is an easy matter, using a Lowry thermo-regulator and circulating the water by means of a small pump, to keep the temperature constant to 1/100°, but differences of temperature less than 1/10° hardly make a perceptible difference in the readings with such dilute solutions as these.

If (as is usually the case) amides and amic acids are present, which have an optical rotatory power, it is advisable to make the solution acid before measuring the rotatory power; for this purpose sulphur dioxide should be passed through the solution, as suggested by Pellet (see p. 44).

of yeast. It is then stoppered with cotton wool and the yeast allowed to incubate for 21 to 28 days at 25°.

After completion of the fermentation, 5 c.c. of alumina cream are added, the solution made up to 100 c.c. at 15°, filtered and 50 c.c. are used for the reduction. The difference between the average reduction with *a*, *b* and *c* and the average of *d* and *e* gives the reduction due to *maltose*.

(4) **Pentoses.**—These are approximately determined in 50 c.c. of A by distilling with hydrochloric acid according to the Tollens-Kröber method (see p. 63).

(5) When the reduction in (1) due to pentose and maltose has been allowed for, using the values for the reducing power of the pentoses given by Daish (see p. 62), the remaining reducing power is due to dextrose and lævulose; the actual proportions of these sugars, *in the absence of other substances possessing a rotatory effect on polarised light*,<sup>1</sup> can be calculated from the reducing power of the solution, combined with its corrected specific rotatory power, as suggested by Brown and Morris.<sup>2</sup>

A simple apparatus for evaporating plant and animal extracts *in vacuo*, such as is necessary in the above scheme of analysis, has been described by the writer. By means of this apparatus all the difficulty encountered with such material, owing to the tendency to frothing which usually occurs, is completely overcome. Large volumes of liquid can be evaporated continuously and the distillate recovered, if necessary in fractions; the apparatus requires practically no watching after the distillation has once been started and can be left to itself whilst other work is proceeded with. It is only necessary from time to time to renew the liquid in the distilling flask A, by means of the dropping funnel A'.

The apparatus consists of an ordinary distilling flask with the side-tube bent up and passing into a wide piece of glass tube B which serves as a froth-trap; the latter is connected by glass tubing with the condenser D, the lower end of which passes through a rubber stopper into the cylindrical dropping funnel E, which in turn is connected, as shown, below with the pump flask G and above with the large reservoir P, which serves to take up small variations of pressure and thus ensure a steady vacuum throughout the system. In this way regular ebullition, without overheating or frothing, is secured.

The vacuum is maintained by means of an ordinary water injector-pump, connected through a Hutchinson regulating valve *J* (*Chemical News*, 1912, 99) with the bottle *H* and thence with *E* and *G*; a glass cock is interposed at *T*, whilst *S* is a screw-clamp which operates on the piece of rubber pressure-tubing connecting *G* and *H*. At *M* a manometer tube is inserted which shows the vacuum throughout the system. The Hutchinson valve takes up large

<sup>1</sup> Such substances are asparagine, glutamine, aspartic and glutamic acids, which occur widely in plant material and are not removed in the ordinary process of treatment by basic lead acetate, etc.; these substances are likely to cause error in the estimation of sugars in plant extracts and in materials such as beet-sugar molasses.

<sup>2</sup> *Trans.*, 1893, 63, 604.

<sup>3</sup> *J. Agric. Sci.*, 5, 434; *Chem. World*, 1914, 3, 239.

variations in the vacuum due to changes of water pressure, so that by means of this, combined with the regulating reservoir *P*, changes in the vacuum are reduced to a minimum.

When the liquid in *A* first begins to boil there is often a great tendency to froth; should this occur, the froth rises into the trap *B*, breaks against a disc of copper-gauze, and the liquid is returned automatically to the flask through the piece of glass tube *L*.

The combination *E* and *G* allows of the distillate being removed from time to time; whilst the distillation is proceeding, the vacuum in *G* is main-

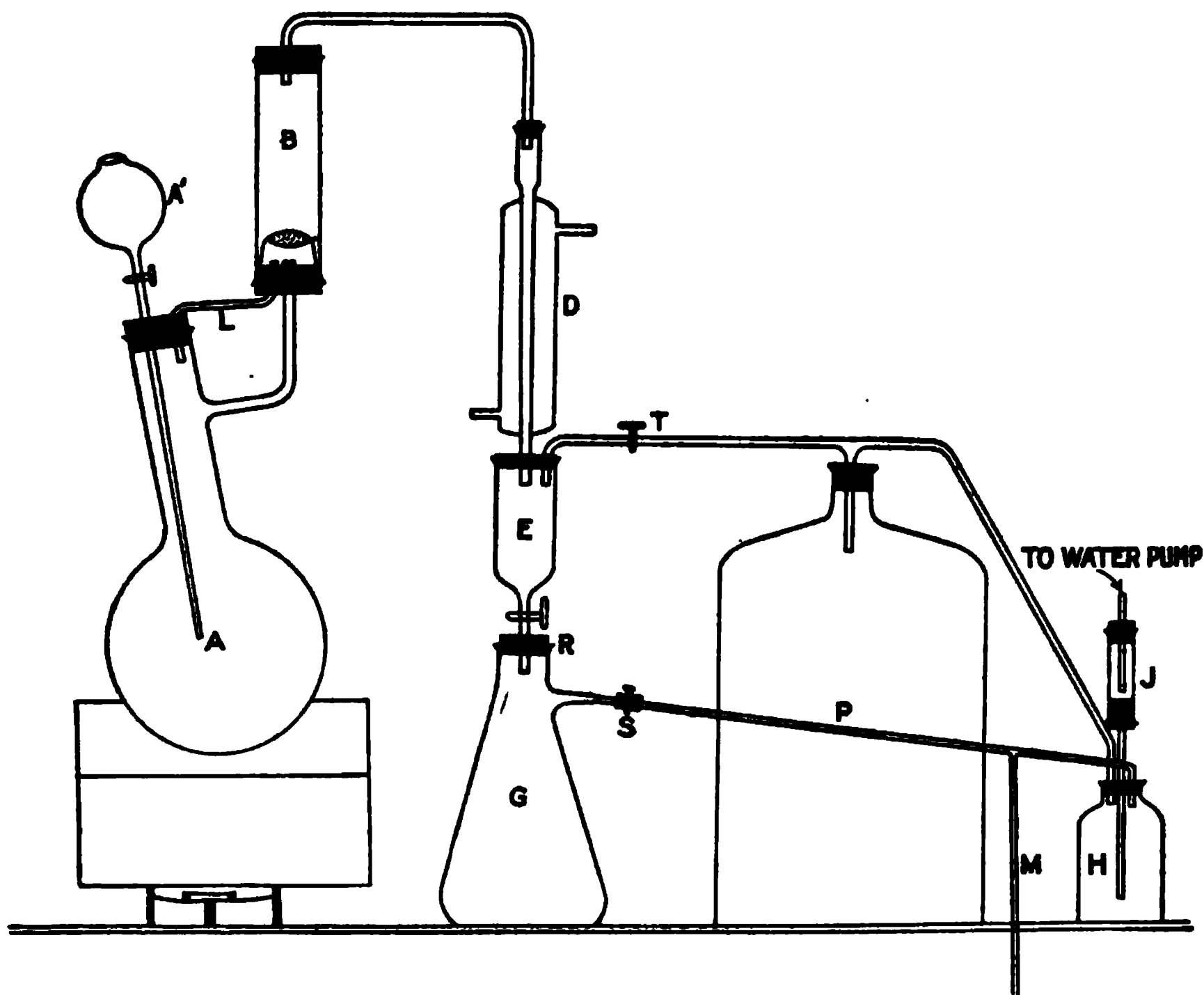


FIG. 2.

tained the same as in the rest of the system so that by opening the glass tap of *E* the distillate runs down into *G*. When *G* is full and it is required to empty it, the cock *E* is closed and the screw-clamp of *S* screwed down to the rubber pressure tube. The latter is then detached from the side tube of *G* and the flask *G* removed from the rubber stopper *R*, emptied and replaced without interfering with the vacuum throughout the rest of the system. After it has been replaced, *S* is opened and in a very short time the vacuum is reestablished in *G*, the same as throughout the rest of the apparatus.

It is a simple matter by introducing T-pieces to run two or more of these distilling apparatus in conjunction with a single vacuum pump and a single

regulating vessel *P*. All connections must of course, be made with rubber stoppers or rubber pressure tubing.

### ERRATA IN VOL. I.

Page 286, line 5 from bottom for "proteins" read "protein."

Page 290, line 10 for  $W = \frac{1000W}{D}$  read  $W = \frac{1000w}{D}$ .

Page 290 line 16 for "water" read "solution."

Page 301 for "Levo" read "lævo" throughout.

Page 303, in the table, under "Milk Sugar" insert "anhydrous." In the milk sugar column for "67.8" read "78.4," for "55.8" read "55.3."

Under "maltose" for 139.0 read 138.0.

Page 306, in bottom table, insert after "Lactose" the word "hydrate." Insert also: Lactose, anhydrous  $[\alpha]_D = +55.3$ .

Page 311, line 3 from bottom the reference should be "Zeit. Ver. Deut. Zuckerind."

Page 311, line 12 "Diot," should read "Dist."

Page 314 line 16 from bottom for "sentianose" read "gentianose."

Page 318, line 12 for 175 read 173.

Page 319, line 4 from bottom for "0.0678 grm. lactose" read "0.0784 lactose anhydrous."

Page 322, line 6, from bottom for "two" read "ten."

Page 323, line 2, for "detail is" read "details."

Page 328, the table at head of page 328 should be amended as follows:

	Glucose, $C_6H_{12}O_6$	Cane sugar, $C_{12}H_{22}O_{11}$ (after inversion)	Lactose, $C_{12}H_{22}O_{11} + H_2O$	Lactose (anhyd.), $C_{12}H_{22}O_{11}$	Maltose, $C_{12}H_{22}O_{11}$
Copper, Cu.....	0.5676	0.5392	0.7621	0.7240	0.9155
Cuprous oxide, $Cu_2O$ ..	0.5042	0.4790	0.6769	0.6431	0.8132
Cupric oxide, $CuO$ .....	0.4535	0.4308	0.6088	0.5784	0.7314

As the reducing power of the sugars varies with the amount of sugar present, these tables are only strictly correct for one concentration of the sugar solution. It is therefore more exact to make use of the table of Brown, Morris and Millar (page 27) which gives the reducing power for different quantities of cupric oxide precipitated.

Page 328, line 9 from bottom, transpose "by" and "of."

Page 329, line 9 from "bottom for "formulas" read "formulæ."

Page 330, for "y" read "Y" throughout.

Page 331, bottom-line delete %.

Page 332, line 20 from bottom for "solution" read "solutions."

Page 335, line 11 for "cabonate" read "carbonate."

Page 337, line 8 from bottom, for "has" read "have."

Page 340, line 12 from bottom delete "with."

Page 342, line 20, "matters" should be transferred to 4 lines higher up, before "should," "really" should read "readily."

Page 344, line 6, for "in" read "is."

Page 358, line 12 from bottom for "eight" read "seven."

Page 362, line 17 from bottom, the later value for  $K$  (absolute) of maltose (Brown, Morris and Millar *Trans.*, 1897, 100) is 62.2.

Page 363, line 2 for "reaction" read "solution."

**Page 365**, the value for lactose  $[\alpha]_D = 52.7$  should be  $52.5^\circ$  and refers to hydrated lactose,  $C_{12}H_{22}O_{11} \cdot H_2O$ . For anhydrous lactose,  $[\alpha]_D^{20} = 55.3$ . In line 14 from bottom the reducing power of anhydrous lactose is roughly  $\frac{2}{3}$  that of dextrose.

**Page 375**, line 13 from bottom, read "invert sugar is usually a syrup."

**Page 376**, line 15 from "caclulated" read "calculated;" line 8 from bottom for "percentum" read "percentage."

**Page 387**, line 19, delete "degrees."

**Page 401**, line 8, for "læonlose" read "lævulose."

**Page 401**, line 11 from bottom, for "anhydrid" read "anhydride."



# STARCH AND ITS ISOMERIDES.

BY WILLIAM A. DAVIS.

A study of the methods of estimating starch has recently been published by Davis and Daish.<sup>1</sup> A new method, based on the use of taka-dia-  
stase, has been proposed, which is at once more accurate and more generally applicable than any of the processes which have yet been suggested. The following summary of the paper may here be given.

The modified Sachsse method (Vol I, p. 420), which is Official in the United States of America<sup>2</sup> and is based on the hydrolysis of the starch present with boiling dilute acid, is valueless in the majority of cases when dealing with plant material, because of the presence of pentosans, "hemi-celluloses" and other substances which yield reducing sugars that count as dextrose; even when such substances are absent the method gives results which are more than 5 per cent. low, owing to the destruction of dextrose that occurs during the prolonged treatment with acid which is a feature of this method.<sup>3</sup> In a series of analyses made by this process, of samples of purified potato starch dried *in vacuo* at 120°, results ranging from 93.8 to 94.3% of starch were found, whereas by the ordinary O'Sullivan diastase process an average result of 100.1% was obtained; with taka-dia-  
stase (see p. 72) the average result with the same sample was 99.6%, a value which probably represents the real starch more closely than the figure obtained by the ordinary diastase process, the calculations of which depend upon a value for the specific rotatory power of dextrin derived from observations made with similar material. Carefully purified starch always contains small quantities of protein material, cellulosic tissue and ash, so that the figure 99.6% obtained with the taka-dia-  
stase is probably a close approximation to the percentage of true starch, and the acid process shows a loss of more than 5%. The destruction of dextrose is a source of error in all the methods which make use of hydrochloric acid to effect hydrolysis, such as that of Märcker and Morgen, even when the primary conversion of the starch has been carried out with diastase.

Although ordinary diastase gives with purified starch results by O'Sullivan's method which are approximately correct, values 15 to 20% lower than the actual starch content may be obtained when it is applied to leaf material or plant tissues in general, owing to the loss of dextrin. In the majority of cases, plant material, which has been previously deprived of sugar by prolonged ex-

<sup>1</sup> *J. Agric. Sci.*, 1914, 6, 152.

<sup>2</sup> *Bureau of Chemistry, Bulletin* 107, Revised, 1912, page 53.

<sup>3</sup> Compare *J. Agric. Sci.*, 1913, 5, 437.

traction with alcohol, still contains tannins, amino-acids, proteins, etc.; during the hydrolysis by diastase these pass into solution and exercise a very marked effect on the reducing power and optical activity of the solution. These substances have therefore to be removed by the addition of basic lead acetate, which almost invariably produces a heavy precipitate in the filtered solution obtained from the diastase conversion. Although basic lead acetate *does not of itself precipitate dextrin*, when dextrin is present in solutions in which a precipitate is produced, as in the purification of the solutions obtained from the diastase conversions, it is *carried down with this precipitate and is thus lost to the analysis*.<sup>1</sup>

### Taka-diestase as an Agent in Estimating Starch

To estimate starch in foliage leaves and in similar cases in which it is necessary to purify the solution after hydrolysis has been effected, it appeared probable that the so-called "taka-diestase" would be more suitable than ordinary diastase, as it is said to give rise only to maltose and dextrose (compare Croft-Hill, *Proc. Chem. Soc.*, 1901, 240, 184) free from dextrin.<sup>2</sup> If this were the case, it would be possible to add basic lead acetate or other clarifying agents without losing sugars. The results given in the following table show that this is actually true and that the use of taka-diestase affords an accurate means of estimating starch in cases where the ordinary diastase process is quite unsuitable. The product of the action of taka-diestase on starch consists, after the first three hours, solely of a mixture of maltose and dextrose; as time proceeds the amount of dextrose increases at the expense of the maltose, which is gradually converted by the enzyme maltase present in the taka-diestase, into two molecules of dextrose. The curve given (Fig. 3) shows this. The dextrose curve represents the dextrose formed from 100 grm. of starch, *calculated as starch* (by multiplying the dextrose figure at each period by 0.9), the maltose curve similarly showing the maltose as starch (dividing the maltose figure by 1.055). This system of plotting the results shows for every instant the proportion of the *original starch which is present either as maltose or dextrose*, the sum of the maltose and dextrose values at each point being approximately 100, so that the two curves are complementary.

From the shape of the curves, coupled with the results found after 3 hours, it is probable that the first action of the taka-diestase is to break down the starch to dextrin and maltose, just as in the case of ordinary

<sup>1</sup> When basic lead acetate is added to the solution obtained by the diastase conversion of *purified starch* not the slightest precipitate is produced with the dextrin existing in solution; but results obtained in a series of special experiments showed that if sodium carbonate is subsequently added, or hydrogen sulphide is passed so as to precipitate the lead, a greater or smaller proportion of the dextrin is removed by co-precipitation.

<sup>2</sup> In 1898 Stone and Wright (*J. Amer. Chem. Soc.*, 20, 639-647) attempted to estimate starch by means of taka-diestase; but as they assumed maltose to be the only sugar formed and measured the products of the action solely by the reducing power without reference to their rotation, they concluded that under their conditions "taka-diestase is not adapted for use in the quantitative estimation of starch."

TABLE I.—ACTION OF 0.1 GRM. TAKA-DIASTASE ON POTATO STARCH AT 38°.

Time in hours	Weight of starch dried $\frac{1}{2}$ <i>vacuo</i> at 120°	CuO from 25 c.c. of 500 c.c.	$a_D$ in 200 mm. tube at 20.00°	Dextrose in 500 c.c.	Maltose in 500 c.c.	Total starch	% starch found	Dextrose Maltose	Remarks
3	2.0061 1.9978	0.1321 0.1380	1.192° 1.273	.....	.....	.....	.....	.....	{ Dextrin still present. No alumina cream added.
6	2.0099 1.9914	0.1581 0.1535	1.103 1.097	0.2204 0.1640	1.892 1.932	1.9914 1.9776	99.55 99.34	0.116 0.085	No alumina cream. No alumina cream.
12	1.9752 1.9940	0.1780 0.1800	0.991 0.973	0.5328 0.5748	1.5930 1.5430	1.9884 1.9792	100.7 99.37	0.334 0.372	No alumina cream. 5 c.c. alumina cream.
24	2.0148 1.9876 2.0145 2.0046	0.2189 0.2205 0.2218 0.2212	0.808 0.764 0.783 0.777	1.1596 1.2302 1.2204 1.2218	1.0214 0.9148 0.9534 0.9414	2.0112 1.9739 2.0018 1.9916	99.80 99.33 99.37 99.39	1.135 1.345 1.280 1.298	5 c.c. alumina cream. 5 c.c. alumina cream. No alumina cream. 5 c.c. alumina cream.
	2.0024	0.2167	0.794	1.1546	0.9982	1.9846	99.11	1.157	{ 5 c.c. basic lead added and this pptd. by solid $\text{Na}_2\text{CO}_3$ .
48	2.0000 2.0000	0.2561 0.2544	0.594 0.616	1.8106 1.7674	0.3852 0.4416	1.9942 2.0086	99.71 100.40	4.700 4.002	No alumina cream. 5 c.c. alumina cream.
72	2.0016 1.9961 2.0084 2.0046	0.2588 0.2562 0.2571 0.2568	0.556 0.562 0.569 0.566	1.886 1.852 1.8536 1.8538	0.2874 0.3113 0.3231 0.3178	1.9703 1.9620 1.9741 1.9696	98.45 98.28 98.33 98.27	6.563 5.950 5.737 5.833	5 c.c. alumina cream. 5 c.c. alumina cream. 5 c.c. alumina cream. 5 c.c. alumina cream.
96	2.0000 2.0048 2.0054	0.2592 0.2590 0.2569	0.562 0.572 0.562	1.8838 1.8694 1.8600	0.2992 0.3226 0.3082	1.9790 1.9879 1.9660	98.95 99.15 98.05	6.296 5.794 6.034	5 c.c. alumina cream. Nothing added. 5 c.c. alumina cream.

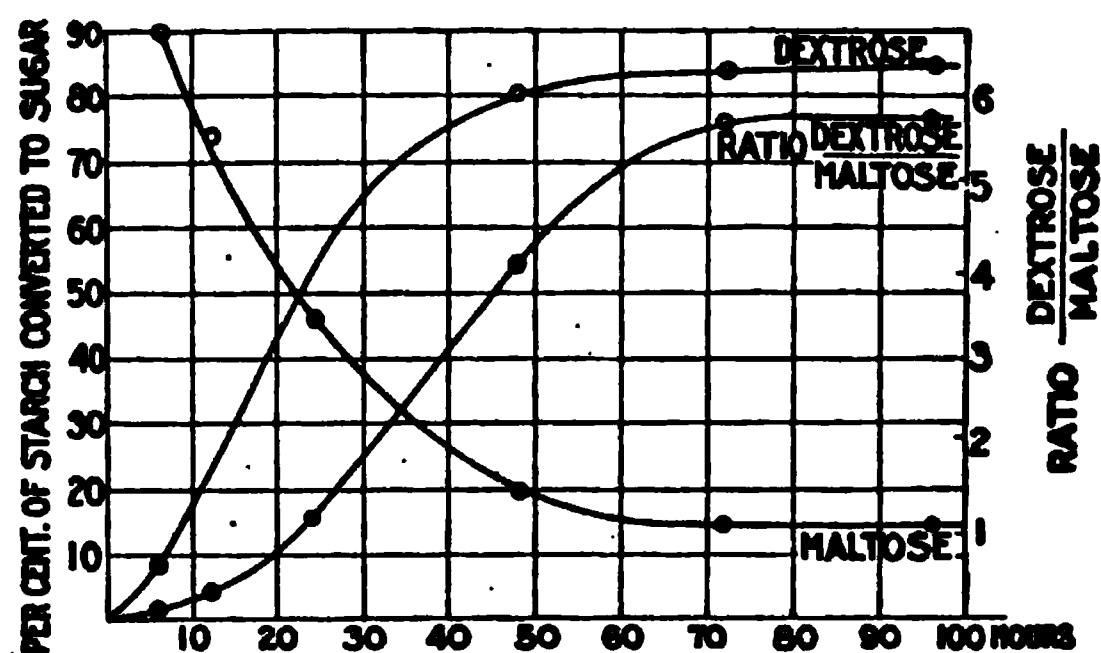


FIG. 3.

diastase; the maltase comes into action comparatively slowly, so that after 6 hours only  $\frac{1}{10}$  of the original starch is present as dextrose. Subsequently, however, the rate at which dextrose is formed increases, following very nearly a straight line curve between 6 hours and 28 hours, when about 60% of the starch is present as dextrose; the rate of formation of dextrose then rapidly slows down until a nearly constant value is reached in the neighbourhood of 84%.

The view that has recently been put forward by Kita,<sup>1</sup> that when taka-diastase acts on starch the dextrose is split off directly from the starch and is

<sup>1</sup> *J. Ind. Eng. Chem.*, 1913, 5, 220.

therefore not formed through the intermediary of maltose, is highly improbable in view of the above results.<sup>1</sup> Davis and Daish give analyses made with maltase-free yeasts confirming the view based on these results, that the actual product of the conversion throughout is a mixture of maltose and dextrose only; after 6 hours every trace of dextrin has disappeared under the conditions employed.

At 55°, the optimum temperature for the action of ordinary diastase, the action of taka-diaastase, at least as regards the transformation of maltose into dextrose, is very much restricted, owing to the fact that the enzyme maltase is gradually destroyed at the higher temperature. In working with taka-diaastase, therefore, a *temperature of 38 to 40° should not be exceeded*. It is noteworthy that the average value for the starch present in the purified potato starch found on using taka-diaastase in the conversions of 6 to 48 hours is 99.65, whereas with ordinary diastase a value generally 0.5 per cent. higher was obtained (see page 70). It is probable that the numbers obtained with taka-diaastase more nearly represent the true starch values, as the calculations are based on the constants for two pure sugars only; they do not involve any assumption with regard to specific rotatory power for the "dextrin" existing in solution, which is generally taken at 202°, although some doubt may still be entertained as to the exactness of this value. It is probable too that the purified potato starch contains a small proportion of foreign material; hence the low value of 99.6%.

When the conversions with taka-diaastase are prolonged beyond 48 hours, somewhat lower starch values are generally obtained, as is seen in Table I; it is possible that some slight destruction of the sugars may occur during these prolonged conversions, but the lower values may also be due to the fact that a larger proportional error is incurred in reading the rotation. In Table I, the actual readings in a tube of 200 mm. for the longer conversions range only from about 0.5 to 0.6°; an error of 0.005° in the reading would therefore represent an error of 1%.

The use of taka-diaastase in starch estimations has the advantage that it gives rise to two *sugars*, maltose and dextrose, the rotatory powers of which have been carefully determined; the temperature coefficients for these are exceedingly small so that no very special precautions to ensure exact constancy of temperature are necessary in ordinary work.

In actual analytical practice it is an easy matter to arrange the quantities so that considerably higher rotations are observed and the proportional error in this direction diminished; if possible, a 400 or 600 mm. tube should be employed. That the addition of precipitating agents such as alumina cream and basic lead acetate and the formation of heavy precipitates, such as are produced with lead by hydrogen sulphide and sodium carbonate, do not in the least influence the results, is shown by the analyses in Table I and numerous other experiments which need not be described.<sup>2</sup>

<sup>1</sup> See Davis, *J. Soc. D. and Col.*, 1914, 7, 249.

<sup>2</sup> Revis and Burnett (*Analyst*, 1915, October) have successfully applied taka-diaastase to the estimation of starch in cocoa, which hitherto presented special difficulties.

### Estimation of Starch by Means of Taka-diastase.

To estimate starch, the dry material (free from sugars<sup>1</sup> and, if necessary, previously extracted with water to remove gums, amylans, etc., see page 75) is gelatinised with 200 c.c. of water in a 250 c.c. beaker flask heated for  $\frac{1}{2}$  hour in a water-bath at 100°. The solution is cooled to 38°, 0.1 gm. taka-diastase added,<sup>2</sup> together with 2 c.c. of toluene and the mixture left 24 hours in order that the conversion may take place; it is then heated in a boiling water-bath to destroy the diastase and the clear solution above the residual material is filtered through a fluted filter paper into a 500 c.c. measuring flask; the residue is thoroughly washed several times by decantation, the washings being passed through the filter paper until the volume of liquid in the flask amounts to about 475 c.c. The necessary quantity of basic lead acetate is then added to precipitate the tannins, etc., present in the solution; the amount required varies considerably with different leaves, generally ranging from 5 c.c. to 25 c.c. A large excess of lead should be avoided and tests should be made after each small addition of lead acetate in order to ascertain when the precipitation is complete. When this is the case the solution is made up to 500 c.c. at 15°, and filtered; 100 c.c. of the filtrate are placed in a 110 c.c. measuring flask, the slight excess of lead precipitated by adding solid sodium carbonate and the volume adjusted to 110 c.c. at 15°. 50 c.c. of the filtrate from the lead carbonate are used for the reduction and another portion polarised in a 400 mm. tube. The following example shows the method of calculation:

Weight of extracted leaf material ( <i>Tropaeolum majus</i> ) after drying in steam oven	= 10.4122 gm.
Weight of leaf material dried <i>in vacuo</i> at 100°	= 9.4059
CuO from 50 c.c. of the final 110 c.c.	= 0.4492 gm.
Polarisation of this solution in 400 mm. tube at 20.00°	= 1.995°
If $x$ = gm. dextrose in 50 c.c. of this solution.	
$y$ = gm. maltose in 50 c.c. of this solution.	

we have, using the values of CuO corresponding to 1 gm. of dextrose and maltose for the weight 0.4492 CuO in the tables of Brown, Morris and Millar:

$$2.369x + 1.362y = 0.4492 \quad (1)$$

For the 400 mm. tube, employing the values  $[\alpha]_D^{20} = 137.6$  and  $[\alpha]_D^{20} = 52.7$  for maltose and dextrose we have also

$$4.216x + 11.008y = 1.995^\circ \quad (2)$$

Solving equations 1 and 2 for  $x$  and  $y$

$$x = 0.1095 \text{ gm. dextrose in 50 c.c.}$$

$$y = 0.1394 \text{ gm. maltose in 50 c.c.}$$

$$\text{Total dextrose in 500 c.c. original solution} = 0.1095 \times \frac{110}{50} \times \frac{500}{100} = 1.2045 \text{ gm.}$$

$$\text{Total maltose in 500 c.c. original solution} = 0.1394 \times \frac{110}{50} \times \frac{500}{100} = 1.5334 \text{ gm.}$$

$$\text{Starch corresponding to dextrose} = 0.90 \times 1.2045 = 1.0840 \text{ gm.}$$

$$\text{Starch corresponding to maltose} = 1.5334 + 1.055 = 1.4535 \text{ gm.}$$

$$\text{Total starch} = 2.5375 \text{ gm.}$$

∴ % of starch in vacuum dried extracted leaf material

$$2.5375 \times \frac{100}{9.4059} = 26.97\%.$$

<sup>1</sup> To remove sugars the material should be thoroughly extracted by boiling 80 % alcohol in a Soxhlet extractor. For the details in the case of leaf material and other vegetable tissue, see Davis and Daish (*loc. cit.*); precautions should be taken in such cases to ensure that all enzymes present are destroyed at the moment the sample is taken.

<sup>2</sup> We have used the commercial preparation of Messrs. Parke, Davis & Co.

### Precautions Necessary in Taking Samples for Analysis.

If the dried, ground plant material is bottled before analysis, it is absolutely necessary when each sample is taken for the analysis, *to turn out the whole of the material on to a sheet of paper and thoroughly mix it before sampling.* If this precaution is not observed and successive samples are taken directly from the bottle, it is frequently found that the proportion of starch present in the material increases toward the bottom of the bottle. This is no doubt due to the fact that the heavier starch grains, set free from the tissue by grinding, sink to the bottom of the bottle, whilst the lighter fibrous material rises to the top. This is well shown by the following successive analyses made with potato leaves (previously freed from sugars by extraction):

1 sample from top of bottle, starch	= 7.54 % on vacuum dried matter.
2 sample from middle of bottle	= 9.19 % on vacuum dried matter.
3 sample from middle of bottle	= 9.23 % on vacuum dried matter.
4 sample from bottom of bottle	= 12.39 % on vacuum dried matter.

When, however, the sampling is carried out in the way described above the agreement between different individual determinations is as satisfactory as could be expected in this class of work.

One of the principal difficulties in estimating starch in plant material is due to the presence of gummy substances, tannins, proteins, etc., which pass into solution during the hydrolysis and exercise an effect on the rotatory and reducing power of the solution. These substances are very largely removed by the use of basic lead acetate, but sufficient impurity remains, even after this treatment, to falsify the analyses in some cases. Thus in the case of mangold leaf a lævorotatory gum is present, which gives an error of nearly 10% on the rotation actually measured.

In working with plant material it is generally possible to extract the disturbing gummy substance prior to the starch conversion by a preliminary treatment with water.<sup>1</sup> Thus in the case of the mangold leaf, by adding 200 c.c. of water and 5 c.c. of toluene to the leaf material and extracting for 24 hours at 38°, decanting and washing with a little water and subsequently converting with taka-diastrase, in the ordinary way, a solution is finally obtained (after the usual treatment with basic lead and sodium carbonate) which in a 400 mm. tube shows a lævorotation of not more than 0.01°. It is noteworthy that the preliminary treatment with water fails to remove the greater part of the material precipitable by basic lead acetate, so that this treatment is necessary even after the preliminary extraction with water.

In the case of plant material from which gummy matter is extracted with extreme difficulty, it would probably be sufficient to introduce a correction for any active substances present by carrying out a control experiment or "blank" in which the diastase is omitted but the material is otherwise treated exactly as in the actual estimation of starch.

<sup>1</sup> Compare Brown and Millar, *Trans. Guinness Lab.*, Vol. I, 79.



### Ewer's Method of Estimating Starch in Cereals.

This is a method which has come into considerable use especially in dealing with brewers' materials (barley, grains, etc.). It is a modification of Lintner's polarimetric method (see Vol. I, page 424) based on the substitution of hot dilute hydrochloric acid for the cold acid used in this process. The following is a description of the process as applied to barley.<sup>1</sup>

The barley is coarsely triturated, and then ground in a Dreef mill to such a degree that the meal passes through a half-millimetre sieve (with the exception of a small quantity of husk which is subsequently mixed with the sifted portion). 5 gm. of the grist are mixed and shaken in a 100 c.c. flask with 25 c.c. of dilute hydrochloric acid (containing 1.124% of hydrochloric acid by weight), the neck of the flask being rinsed down with a further quantity of 25 c.c. of the same acid. The flask is rotated several times and then placed in a boiling water-bath for exactly 15 minutes during the first three of which it is repeatedly rotated. The solution is then made up to about 90 c.c. with cold water, cooled to 20°C., clarified with 2 c.c. of sodium molybdate solution (prepared by fusing 30 grams of pure molybdic acid and 25 grams of pure, dry sodium carbonate, dissolving the product in water to 250 c.c. and filtering) or 10 c.c. of 4% phosphotungstic acid solution, made up to 100 c.c. with water, mixed, filtered and polarised. The solution, after polarisation, may be treated with a few drops of molybdate solution to make sure that all the protein has been thrown down. The starch solutions are very stable, and show no decrease of rotation after standing for 24 hours. The author finds that the specific rotation of barley starch is  $[\alpha]_D^{20} = 181.5^\circ$ . With a half-shadow saccharimeter (Ventzke-Soleil or German sugar scale, and Auer light with a light filter, the percentage of starch is obtained by multiplying the reading of a 5 % solution in a 200 mm. tube by 1.912; the specific rotation of the starch solution is independent of the concentration between the limits of about 1.25–5%. The above method is preferable to those of Lintner and Wenglein in that the use of concentrated acids is avoided; moreover, there is no need to grind the meal very finely. On the other hand, in Lintner's method, heating and cooling the solution are avoided.

For wheat and other cereals the following specific rotations are used for the starch:

Wheat.....	182.7	Rye.....	184.0
Barley.....	181.5	Oats.....	181.3
Rice.....	185.9	Maize.....	184.5
Potato.....	195.4		

Whilst the method may be useful in certain cases for giving comparative results, it is very doubtful whether the values obtained represent the *true starch* present, owing to the fact that the treatment with hydrochloric acid breaks down pentosans and hemicelluloses, substances with a dextrorotation

<sup>1</sup> *Zeits. ges. Brauw.*, 1908, 31, 250.

passing into solution which count as starch; thus the writer found that a sample of mangold leaf, which was absolutely free from starch, when subjected to Ewer's method gave a solution having a strong dextrorotatory power, which corresponded with the apparent presence of 16.5% of starch. Far higher values, too, are obtained by this method for the starch present in grain, such as wheat, than are given by the diastase method, so that it must be regarded as a process the reliability of which is very much open to question.

For the theory of the action of enzymes on starch see Davis (*J. Soc. D. and Col.*, 1914, 7, 249); of the action of acids on starch, *ibid.* and Daish, (*Trans.*, 1914, 105, 2053 and 2065).

### Cellulose.

König and Hühn<sup>1</sup> have carried out a comparative series of estimations of cellulose in typical raw materials by the principal methods which have been proposed and adopted by different workers. The materials tested included beech, oak and pine woods, the bark of these woods, sulphite wood pulp, cotton, flax, hemp and jute. The methods employed were those of Weende-Henneberg ("crude fibre"); of Tollens-Dmochowski (in which hydrolysis according to the Weende-Henneberg method is followed by oxidation with nitric acid); of König (see Vol. I, page 437) using ammoniacal hydrogen peroxide; of Cross and Bevan (chlorination); Schulze (potassium chlorate and nitric acid) and Müller (bromine water and ammonia). Of these methods that of Weende-Henneberg and the direct treatment with ammoniacal hydrogen peroxide give products which cannot be described as cellulose, being still rich in lignin, whilst others yield celluloses more or less profoundly affected by the oxidising agents employed and still containing appreciable residues of the non-cellulose constituents of the raw material. Consequently, the authors made investigations of the nature of the "cellulose" products obtained, not only by qualitative tests, which are of little real value, but by quantitative determinations of elementary composition, calorific value, methyl value, and yield of furfural (pentosans). Comparison of the values so obtained with those given by the original material throw light on the extent to which non-cellulose groups have been removed. Considerations of such data raise the question of a definition of cellulose. According to König and Hühn the original material contains "true cellulose," lignin, hemihexosans and pentosans, together with cutin in the case of bark tissue. They contend that only by a regulated hydrolysis followed by oxidation can the "true cellulose" be freed from the other constituents. Methods depending upon oxidation without hydrolysis (for example, Cross and Bevan's chlorination method) may under favourable conditions eliminate the greater part of the lignin, but such methods as a rule fail to remove most of the hemihexosans and

<sup>1</sup> *Zeit. Farb. Ind.*, 1911, 11, 297, 326, 344, 366; 1912, 12, 4, 17, 37, 57, 77 and 102.



pentosans and the higher yields so obtained depend upon the presence of these impurities; moreover, the cellulose obtained has pronounced oxycellulosic properties. For instance, Cross and Bevan's method yielded 100% of cellulose from cotton, whilst König's method gave only 88.27% in the form of a friable powder. Hence it is contended, cotton is not substantially composed of true cellulose but contains considerable proportions of hemihexosans.

König and Hühn suggest the following method of testing the purity of the preparations of cellulose: The cellulose is dissolved in a solution of zinc chloride in concentrated hydrochloric acid and the liquid examined polarimetrically at intervals over a considerable period, the specific rotatory power being calculated. This gradually rises from zero as hydrolysis proceeds, reaching a maximum after 2 or 3 days, then falling slowly, owing to condensation until the liquid becomes opaque. Cotton cellulose prepared by König's method showed a maximum  $[\alpha]_D = 82.5^\circ$  after 72 hours whilst cotton purified by Cross and Bevan's method showed a maximum of only  $56.7^\circ$  after 55 hours.<sup>1</sup> Hydrocellulose and oxycellulose reach only low maximum rotations and the rotation changes rapidly. König and Hühn consider that this supports the view that digestion with glycerin containing 2 grm. of sulphuric acid per 100 c.c. at a temperature of  $137^\circ$  whilst eliminating the hexosans and pentosans has practically no effect on the "true cellulose" and that König's method in spite of the low yields of cellulose obtained is the best method of estimating that constituent. Next to this method that of Tollens-Dmochowski is preferred; the hydrolysis of the hexosans and pentosans is, however, not complete.

Cross and Bevan<sup>2</sup> have pointed out that the chlorination process when properly controlled shows a minimum of secondary oxidising action being confined to a specific chlorination of the lignin groups. The "crude fibre" methods favoured by König and Hühn yield residual products of degradation by treatments more or less arbitrary because they are relatively non-selective in their actions, which are ill-defined through the complex and unascertained relation of the products to the parent substance. The manipulation, moreover, is too lengthy for technical purposes. Cross and Bevan consider that the chlorination process will remain the standard method of estimating cellulose.

Processes for the estimation of cellulose are necessarily at the present time of a purely conventional character; and for any special purpose in the textile industries a method which corresponds as closely as possible with the condi-

<sup>1</sup> It is doubtful whether any value can be attached to observations of this kind, in view of the extraordinary variations in the specific rotatory power of dextrose (one of the products of hydrolysis in such experiments) with changes of concentration of the hydrochloric acid and difference of temperature. As the question is essentially one of velocity of action, results of even comparative value can only be obtained if such factors as temperature, concentration, etc., are maintained rigidly constant. The extraordinary differences which are found in the rate of destruction of dextrose by hydrochloric acid of different concentration, as well as in the synthetic action of the acid on the sugar are also factors militating against its use for such comparisons (cf. Daish, *Trans.*, 1914, 105, 2053).

The physical condition of the material will also largely determine the relative rate of formation of cellobiose, dextrose and its decomposition products, upon which the maximum reached depends.

<sup>2</sup> 8th Intl. Congress App. Chem., 1912, Sect. VI A, 13, 101; *Zeit. Farb. Ind.*, 1912, 11, 197.

tions and yields of actual practice will probably be preferred. In such cases, "true cellulose" is still a substance to be defined. For the majority of purposes, there is little doubt that the chlorination process gives the most useful and most easily comparable data.

#### ERRATA IN VOL. I.

Page 406. The value  $-24^{\circ}$  given for  $[\alpha]_D$  of  $\alpha$ -amylan is really that of  $[\alpha]_j$ . The latest value of  $[\alpha]_D$  is  $21.6^{\circ}$  (Brown and Millar, *Trans. Guinness Research Lab.*, p. 313). The value given for  $[\alpha]_D$  of  $\beta$ -amylan is also that of  $[\alpha]_j$ ; Brown and Millar give  $[\alpha]_D = -129.7^{\circ}$ .

Page 410, line 5 from bottom for "comparision" read "comparison."

Page 419, line 15 from bottom, delete "a" at end of line.

Page 423, line 15 from bottom insert semicolon after "boiled."

Page 434, bottom line, for "hyoxide" read "hydroxide."

Page 435, line 15 from bottom delete "sub."

Page 445, line 2, delete "appl."

Pages 446 and 447 should be interchanged. In table on page 447, right-hand bottom corner, "page 392" should read "page 435."

Page 449, line 5, "Keldahl" should read "Kjeldahl."

Page 459, line 7, for "Blythe" read "Blyth," line 6 from bottom, delete final "to."

# PAPER AND PAPER-MAKING MATERIALS.

By RALPH H. McKEE.

**Bursting Strength.**—The Mullen's paper tester<sup>1</sup> has been much improved by substituting a lever movement for the milled screw formerly used in fastening the paper. This change almost totally eliminates the personal equation formerly evident in working with this instrument.

In testing thin papers with this instrument the better practice is to use a thickness of four sheets and report one-fourth of the "points" (pounds per square inch bursting strength) obtained as the strength of the paper.

**Thickness.**—In measuring thickness of ordinary and thin papers it is becoming customary to take one-fourth of the thickness shown by the micrometer when four sheets are measured. This takes account of the "grain" of the paper and gives a result more nearly according with the result obtained when the paper is put into reams or into book form.

**Sizes and Weights.**—American practice differs much from the English in regard to sizes and weights of flat papers. In Canada the English practice is given the preference. Standard American sizes in inches are as follows:

Flat letter.....	10 × 16	Medium.....	18 × 23
Small cap.....	13 × 16	Double small cap.....	16 × 26
Flat cap.....	14 × 17	Royal.....	19 × 24
Demy.....	16 × 21	Double cap.....	17 × 28
Folio.....	17 × 22	Super royal.....	20 × 28

In America the 500 sheet ream is most commonly used though the 480 sheet ream is still used to some extent. The English 516 sheet ream is never used. The American "standard ream" of 24 × 36 in. is customarily used as a basis in calculating costs and in giving orders to the manufacturing departments.

**Sulphate and Sulphite Fibres.**—It has lately been found that undercooked sulphate fibre makes extra strong papers ("kraft" papers) such as are wanted for wrapping and envelope papers, a field previously controlled by unbleached sulphite fibre and the more expensive manila fibre. It is thus often desirable to see if a paper is a true "kraft" or whether it is partly or wholly a sulphite product. The following efficient method of distinguishing these two fibres we owe to Schwalbe.

Disintegrate the paper by a rasp or grater and remove rosin by extracting with alcohol and ether. Dry a small amount of the pulp. Heat it at 60 to 80° with 15 c.c. of *N*/20 ferric chloride for 10 minutes and the

<sup>1</sup> Vol. I, Fig. 76, 4th ed.

pulp will settle to the bottom of the beaker. Remove and reject all pulp adhering to the sides of the vessel. Filter and wash the remainder with warm water until no iron shows on testing the washings. Put the drained fibres in a small beaker, add 10 c.c. of 1% sulphuric acid and then 6 to 8 drops of a 2% solution of potassium ferrocyanide. Heat 5 to 10 minutes at 60 to 80° to bring out the colour. Wash and estimate by examining under the microscope the relative proportions of each kind present, counting the differently coloured fibres. The fibres of sulphite (unbleached) product are coloured a deep blue and those of "kraft" sulphate paper a faint yellowish, greenish or bluish colour.

It may be mentioned, though not ordinarily of interest when working with "kraft" papers, that bleached sulphite paper shows mostly pale blue but some deep blue fibres, soda paper pale blue and bleached sulphate uncoloured or faintly blue fibres.

### Wood-pulp.

Four distinct methods are employed in the manufacture of wood-pulp, namely, the mechanical or ground wood, the sulphite, the sulphate and the soda process. The varieties of wood which commonly serve as raw materials are spruce, hemlock, poplar, white fir, balsam, pine and beech. Spruce is the most important of the pulp woods. Nearly 50% of the supply is converted into mechanical wood-pulp; the remainder being "reduced" by the sulphite process. Of the hemlock over 90% is manufactured into sulphite pulp, the other 10% being divided between the mechanical and soda processes. The wood structure of poplar and of beech is such that these woods are readily "reduced" by alkalis, and they are generally converted into soda pulp. The sulphate mill uses any coniferous wood, preference being given to spruce. White fir, balsam, and pine, can be converted by any process and consequently are used by the nearest mill irrespective of its type.

**The soda process** for the manufacture of wood-pulp, the oldest of the chemical methods employed for isolating the pulp fibre, consists in the digestion of deciduous woods with a hot solution of sodium hydroxide. The wood chips should be uniform in size, averaging 1 in. in length. It is unnecessary to remove knots, rotten places, or sawdust, because of the solvent action of the alkali. The chemical action of hydrolysis of the intercellular material gives rise to many organic compounds chief among which are the sodium salts of acids of the acetic series. The hydroxide is prepared by treating a solution of sodium carbonate, leached from "black ash," with milk of lime. The loss in sodium salts during the process is replaced by the addition of commercial soda ash.

Sindall and Bacon<sup>1</sup> give the following table showing the equivalent weights of recovered ash and of lime calculated from their percentage purity.

<sup>1</sup> *Paper Makers Monthly Magazine*, Aug., 1914.

## EQUIVALENT WEIGHTS OF RECOVERED ASH.

% Na <sub>2</sub> O	Tons	Cwt.	Qr.	Lb.
48	100	0	0	0
46	104	6	3	23
44	109	1	3	8
42	114	7	2	6
40	120	0	0	0
38	126	6	1	7
36	133	6	2	18

## EQUIVALENT WEIGHTS OF CAUSTIC LIME.

% CaO	Tons	Cwt.	Qr.	Lb.
100	100	0	0	0
98	102	0	1	18
96	104	3	1	2
94	106	7	2	17
92	108	13	3	19
90	111	2	0	26

These tables show the necessity of a close control of the causticising since a slight change in purity involves a considerable change in weights used. For example, if the percentage of Na<sub>2</sub>O in the recovered ash changes from 48 to 40% one-fifth more weight of recovered ash will be required for causticising. In American practice it is customary to estimate the amount of soda ash in the black ash from the sp. gr. of its aqueous solution, but the same relationship between purity and amount used obtains.

The chips and liquor (8 to 10° Bé. NaOH) are introduced into either a stationary or rotary digester, the manhole closed and steam introduced until the charge is brought up to the maximum cooking pressure. This value varies in different mills but an average would be 100 pounds steam pressure. The maximum cooking pressure is maintained during from 3 to 7 hours depending on the quality of pulp desired. By increasing the time of cooking the yield is decreased but the pulp is of better quality, easier bleached and freer from shives.

At the close of the cooking the digester pressure is reduced to 30 pounds and the charge "blown" into the "blow-pit." The "black liquor" is allowed to drain thoroughly and the crude pulp is transferred to bins provided with false bottoms, in which it is washed free from alkali.

By increasing the cooking pressure the yield of pulp is reduced but the total time of cooking is shortened so that one factor offsets the other. Increase in the concentration of the sodium hydroxide, within limits, decreases the yield but improves the quality of the pulp.

**Analysis of Soda Ash.**—A 10 gm. sample is dissolved in 100 c.c. of water and 10 c.c., equivalent to 1 gm., are withdrawn by a pipette and introduced into a vessel for titration. A few drops of methyl-red or methyl-orange are added and the solution titrated with *N*-hydrochloric or sulphuric acid. The number of c.c. of acid used multiplied by 3.1 gives directly the percentage of Na<sub>2</sub>O. If it is desired to report as Na<sub>2</sub>CO<sub>3</sub> the titration multiplied by 5.3 gives the percentage.

**Analysis of “Black Liquor.”**—E. Sutermeister<sup>1</sup> recommends the following method of analysing the highly colored “black liquors.” To 300 c.c. of water containing 15 c.c. barium chloride (40 per cent.) add 25 c.c. of black liquor. Titrate with normal acid determining the end point by removing a drop at intervals and allowing it to fall into a thin layer of a dilute solution of phenolphthalein contained in a beaker. When the drop no longer produces a pink colour the action is considered complete and the number of c.c. of acid used multiplied by 0.04 gives the weight of hydroxide present.

A second test is made by evaporating 25 c.c. of the liquor to dryness and burning off the organic matter. A titration is then made with normal acid using methyl-orange as the indicator. The difference in c.c. of acid between the two titrations multiplied by 0.053 gives the sodium salts of the carbon acids calculated as  $\text{Na}_2\text{CO}_3$ .

**Lime** used for the manufacture of soda pulp should be nearly pure calcium oxide 1.5 per cent. of silica, iron and alumina and other impurities is the ordinary maximum allowed, nor should the lime be air slaked.

**The sulphate process** for the manufacture of chemical wood-pulp is similar in principle to the soda process, differing however in the fact that the loss of sodium salts during the process is replaced by the introduction of crude sodium sulphate “salt cake,” instead of by sodium carbonate. The salt cake, in a granular form, is introduced into the calcining furnace, where the “black liquor” is being burned to “red ash.” The sodium sulphate reacting with the carbonaceous material present is reduced to sodium sulphide. As a result of incomplete reduction the product is contaminated with a varying percentage of sodium sulphate.

This ash, a mixture of sodium sulphide, sulphate, silicate and carbonate is dissolved in water and causticised with lime to produce the “white liquor” with which the wood is cooked. In practice a measured quantity of unrecovered black liquor is introduced into the digester together with the white liquor. This is especially true when the pulp is not to be bleached. The length of cooking is slightly longer than that required for soda pulp but a longer and stronger fibre is produced.

Sulphate pulp is often of a brown colour and difficult to bleach but being particularly adapted to the manufacture of wrapping papers finds a ready market as an unbleached pulp. Originally “kraft” was a brown paper made from a slightly undercooked soda or sulphate pulp but the term has been so much abused that its present meaning is any strong paper, irrespective of colour, made from sulphate or sulphite fibre.

**Red Ash and White Liquor.**—The total alkalinity of the “red ash” or of the “white liquor” can be measured by dissolving a sample in water and titrating with normal acid using methyl-orange as indicator. The estimation of sulphides, sulphites, thiosulphates and sulphates in the solution presents great difficulty.

<sup>1</sup> *Eighth Intern. Congr. Appl. Chem.*, Vol. 13, p. 265.

W. Field<sup>1</sup> suggests distilling a sample with magnesium chloride in an atmosphere of carbon dioxide and collecting the hydrogen sulphide evolved in a solution of  $N/10$  iodine. The excess of iodine solution is estimated by titration with sodium thiosulphate and the percentage of sulphide then estimated.

Hydrochloric acid can now be introduced into the same solution and the sulphite will be decomposed with the evolution of sulphur dioxide which is passed into  $N/10$  iodine and the titration made as in the case of sulphides. Thiosulphates are estimated in a fresh sample by first titrating with  $N/10$  iodine which converts sulphides to sulphur, sulphites to sulphates and thiosulphates to tetrathionates. The tetrathionate is decomposed in an atmosphere of carbon dioxide with nascent hydrogen, generated from aluminum and hydrochloric acid, and the hydrogen sulphide evolved collected and estimated as in case of sulphides.

A second somewhat similar method by Richardson and Aykroyd<sup>2</sup> gives perhaps more accurate results but is longer.

Carl Moe<sup>3</sup> suggests a rapid method of estimating the sulphide alone. A 1 c.c. sample is titrated with a solution of silver nitrate, added slowly and with repeated shaking until the precipitation of black sulphide ceases and a turbidity in the solution just disappears. The titration should be performed over a white surface to obtain the best results. The writer suggests a solution containing 55.81 gm. of metallic silver or 87.89 gm. of silver nitrate to the litre. 1 c.c. of this solution is equivalent to 1 pound of sodium oxide ( $\text{Na}_2\text{O}$ ) to the cubic foot of solution.

**Sulphite pulp** is produced when small chips of wood are treated at a high temperature and pressure with calcium hydrogen sulphite solution. The chips should be uniform in size, free from bark and sawdust, their length depending on the method of cooking to be employed. In general a longer chip can be employed for the manufacture of an unbleachable pulp than in the case of one to be bleached. The best results are obtained when dry wood is employed, although it is possible to "cook" green wood.

The "acid" used is an aqueous solution of calcium and magnesium hydrogen sulphites in which is dissolved an excess of sulphur dioxide. The acid is prepared by burning either sulphur or iron pyrites and absorbing the gas in cold milk of lime. In burning either, close control over the admission of air should be exercised. Too rapid introduction of air, or leaks in the absorbing apparatus, always results in the formation of sulphur trioxide and consequent loss in efficiency. Furthermore a deposit of calcium sulphate forms in the pipe lines and clogs them. If the supply of oxygen is insufficient for complete combustion sulphur distils over and is deposited throughout the system; this must later be removed.

There are two distinct systems of acid making, the limestone tower and

<sup>1</sup> *Dic. Chem. Ind.* (1898), 372.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1896, 15, 171.

<sup>3</sup> *Paper*, 1914, 14, No. 22, 19.



the milk of lime system. In the limestone tower system, blocks or lumps of dolomite or of limestone are charged into towers or tanks. Water enters at one end while sulphur dioxide gas is introduced and finished liquor is discharged from the other. In the milk-of-lime system, lime milk is introduced into the towers or tanks and sulphur dioxide gas bubbles through it. In some systems the gas produced by burning sulphur is materially strengthened by the introduction of gas relieved from the digester. In others the relief gas is introduced into the acid liquor storage tanks.

The digestion of the wood is effected by two well-defined methods, the *Mitscherlich* or "slow cook" and the "quick cook." The former is used extensively in Europe while the latter conforms more commonly to American practice. In the slow cook the wood is steamed for a period, after which the acid liquor is introduced and the actual digestion takes place; the heating being by indirect steam. At the beginning of the cook it is possible to introduce live steam to hasten the action. In making a quick cook the acid and chips are introduced together into the digester, the cover securely fastened and live or superheated steam introduced until the maximum conditions of temperature and pressure are obtained. These are assigned values, since they vary with the different grades of pulp that a mill may produce, but are constant for any single grade.

The pulp from the digester is thoroughly washed, screened and made into laps or folds for "unbleached," or passed into bleachers if it is to be made into "bleached" sulphite pulp.

Sulphite pulp possesses a long, strong fibre and is used largely in the manufacture of wrapping papers and as a binder for mechanical fibre in newspaper. The bleached sulphite is used in the manufacture of writing papers and for similar purposes.

**Acid Liquor.**—The percentage of free sulphur dioxide is estimated by introducing a 1 c.c. sample into a volume of not less than 100 c.c. of water. A few drops of phenolphthalein are added and the solution titrated with  $N/10$  sodium hydroxide. The number of c.c. of alkali used multiplied by 0.32 gives the percentage of free sulphur dioxide in the liquor.

The total sulphur dioxide is estimated by titrating a 1 c.c. sample diluted with water as in the preceding case with  $N/10$  iodine using starch as indicator. The number of c.c. used multiplied by 0.32 gives the percentage of total sulphur dioxide. The combined sulphur dioxide is obtained by subtracting the percentage of free from the percentage of total sulphur dioxide.

**Pyrites** vary in sulphur content from 35 to 50%. It is therefore necessary to value each parcel on the basis of available sulphur. A sample, finely ground, is treated with nitric acid and bromine water to oxidize the sulphur to sulphate. The volume is then rendered large to prevent occlusion of iron and a 10% solution of barium chloride introduced into the boiling



solution as precipitant. The barium sulphate is filtered off, dried and weighed and the percentage of sulphur present estimated.

**Sulphur** can usually be purchased with a guarantee of from 98.5 to 99% purity. It is seldom analysed, although it is customary to check the moisture content. This is done by drying a 10 gm. sample *in vacuo* over sulphuric acid to constant weight.

**Lime** should contain a high percentage of magnesium. This is because magnesium has a higher combining value, *i.e.*, lower atomic weight, than calcium and because the sulphites and sulphates of magnesium are more soluble than those of calcium. Impurities in lime which affect adversely the quality of paper pulp are iron and silica. A lime of good quality gives the following analysis: CaO 56%, MgO 42%,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  0.5%,  $\text{SiO}_2$  1.0%,  $\text{CO}_2$  and volatile matter 0.5%. For a limestone tower system the same conditions apply and the same impurities are detrimental to the quality of the pulp.

**Sulphate in acid liquor** is usually estimated by adding to a 25 c.c. portion of the liquor 10 c.c. of pure hydrochloric acid, heating the solution to boiling and adding drop by drop 15 c.c. of 10% barium chloride. The precipitation of calcium sulphite is prevented by the strong acid. The precipitate is filtered, washed, ignited and weighed. Convert by factor to per cent.  $\text{CaSO}_4$ . In this estimation the amount of sulphate is reported either as pounds per digester charge or as grains per gallon of liquor.

**Sulphur dioxide in gas** is estimated by means of an Orsat apparatus using sodium hydroxide as an absorbing agent. The use of mercury in the measuring burette may be omitted if water thoroughly saturated with sulphur dioxide is substituted.

**Oxygen.**—In order to regulate the draughts in the burner it is often advisable to know the percentage of oxygen in the gas since this is always a diluent and may cause loss in sulphur by oxidising some of the gas to the trioxide. This estimation is made with the Orsat apparatus, alkaline pyrogallic acid solution being used as an absorbing agent, after the sulphur dioxide is removed by the sodium hydroxide.

**Iron in Pulp.**—Iron is always present to varying extents in pulp. In order to keep this value at a minimum the pulp should be examined for specks of iron. The sheet is held between the observer and a bright light and suspicious places are marked with a pencil. The pulp is cut open until the particle is exposed, two drops of nitric acid are added and a drop of a 10% solution of potassium ferrocyanide or of potassium thiocyanate, when the presence of iron will be evident. The presence of shives is noted by holding the pulp sheet to the light and reporting the number in the average sheet.

**Mechanical or ground-wood pulp** is produced by grinding a log against the surface of a revolving stone. The logs are placed parallel to the axis of the stone, against the periphery of which they are held by hydraulic pressure. The quality of the pulp depends on the uniformity of the fibres and

its freedom from bark, shives and mechanical dirt. There are five factors<sup>1</sup> that influence the quality of mechanical pulp: (1) the proper dressing of the surface of the stone, regulating sharpness and grit; (2) the pressure with which the wood is held against the revolving stone; (3) the peripheral speed of the stone; (4) the temperature of grinding; (5) the quality of the wood employed.

When the stone is very sharp the fibres are literally ground to pieces, a large percentage of shives or slivers is made, and the pulp produced is of extremely short fibre. With a dull stone a pulp with long fibre and few shives is produced, although a greater expenditure of horse-power is required. The effect of increase in pressure in the cylinder and of increase of peripheral speed of the stone are identical. The production of pulp is increased and the strength factor and horse-power per ton of pulp are reduced. Change of peripheral speed is far less effective than increase in pressure.

The question of temperature is differently considered by European and American manufacturers. The cold grinding process producing a fine pulp, free from shives and quite opaque is extensively used by European manufacturers. American practice consists of hot grinding which produces long and strong fibres. In cold grinding about 500 pounds of water are used to one of pulp; in hot grinding the ratio is 50 to 1. The effect of quality of wood is obvious and requires no comment.

Mechanical pulp is used principally in newspapers where strength and permanence are not important factors. It also finds use in the manufacture of wall board and products of similar character. The pulp has a slightly yellow colour and is bleached only with great difficulty and at high comparative cost, so that bleaching is seldom attempted. The yellow colour is counteracted by the addition of dyes, either blue alone or red and blue.

A typical newspaper furnish would be: mechanical pulp 675 pounds, sulphite pulp 225 pounds, talc 45 pounds, clay 45 pounds, soluble blue 4 ounces, rhodamine  $\frac{1}{2}$  ounce.

Paper pulps are characterised as easy or as hard bleaching according to the amount of chloride of lime required to bring the pulp to a standard colour or quality. An easy bleaching pulp has been defined as any pulp that will bleach with 12% or less of bleaching powder.<sup>2</sup>

The action of the bleach liquor is on the ligneous matter left in the wood after the digestion, to oxidise and destroy it. An excess of bleach liquor attacks the cellulose itself forming oxycellulose, which is of no value as a fibrous material.

Heinz C. Lane<sup>3</sup> suggests the following qualitative tests based on the fact that oxidising agents such as potassium permanganate, hydrogen peroxide and potassium dichromate produce a red colour with the organic matter other than cellulose in pulp. The test consists in pouring a definite quantity, 3 or 5 c.c. of a solution containing 0.25 gm. of  $K_2Cr_2O_7$  and 10 c.c. of *N*-hydro-

<sup>1</sup> U. S. Forest Service, *Bul.* No. 127.

<sup>2</sup> *Pulp and Paper Magazine of Canada*, 1914, 12, 203.

<sup>3</sup> *Pulp and Paper Magazine of Canada*, 1914, 12, 430.

chloric acid to the litre, on to uniform samples of pulp and allowing them to stand for 2 to 3 minutes when the colour will have developed. From the shade developed the amount of bleach necessary can be estimated.

Sindall and Bacon<sup>1</sup> suggest the use of a tintometer for measuring shades and that these be made permanent by matching them on porcelain plates so that a permanent and uniform standard may be maintained.

It is often necessary to know the exact point to which the action in the bleaching vat has progressed. To this end titrations of the bleach liquor should be made at intervals of 1 hour at the beginning of the bleaching, progressively shortening to 15-minute intervals toward the end the values should be plotted with time as ordinate and either grains of bleach liquor or c.c. of arsenious acid solution as abscissa.

The method of titration consists of withdrawing 50 c.c. samples with a pipette and introducing them into a casserole. A few drops of starch potassium iodide solution are added and the solution titrated with  $N/10$  arsenious acid until the blue colour disappears.

**Making of Sulphite Pulp.**—The process is controlled by analysis of the digester liquor for contained sulphur dioxide. At intervals of an hour during the first part of the "cook," and at increasingly shorter intervals as the "cook" progresses, a portion of at least 600 c.c. is drawn from the sample tap on the side of the digester. From this hot sample 5 c.c. are quickly added by a pipette to a volume of cold water of not less than 250 c.c. The sulphur dioxide is estimated by titrating with starch and  $N/10$  iodine. The percentages of sulphur dioxide found determine the time of emptying the digester.

More than 0.40%; the pulp is not ready for emptying.

0.38 to 0.34; the pulp *can* be emptied but is somewhat coarse.

0.32 to 0.27; the pulp is ready if not required for bleaching.

0.26 to 0.13; the pulp is ready if required for bleaching.

0.11 to 0.05; the pulp begins to become discoloured.

0.03 to 0.02; the pulp is "burnt."

The method is approximate in that there is a considerable loss of sulphur dioxide from the hot solution, but the loss is nearly constant and so the method has been found satisfactory in practice. A few workers avoid this error by drawing the sample through a water-cooled condenser. The percentages obtained by this last method of sampling are very materially higher.

**Special Tests.**—The following should be consulted by those interested in the subjects indicated as the space available does not permit their detailed discussion here.

A method of measuring numerically the "handle" (German "Griff") of a paper. Briggs, *Papier Fabr.*, 1914, 12 (Convention Number 25a), 27.

Testing the beating time of pulp. Stark, *Papier Fab.*, 1913, 11, 1358.

The copper figure and the true acid figure of sulphite and other cellulose as

<sup>1</sup> *Pulp and Paper Magazine of Canada*, 1914, 12, 203.

a measurement of the dyeing, sizing and bleaching qualities of a pulp. Richter, *Pulp and Paper Mag. Can.*, 1914, 12, 193.

**Specifications.**—The following is a specification of a paper for the United States Government and is typical of American practice.

Machine-finish Printing Paper No. 1.

(12,000,000 pounds to be supplied in rolls and flat of specified standard sizes.)

**Weight.**—25 × 40 in., 500 sheet; 44 pound basis (ream).

**Thickness.**—Shall not exceed 0.0035 in.

**Strength.**—Shall not be less than 12 points (as given by the Mullen bursting strength tester).

**Stock.**—May be bleached chemical wood, free from unbleached or ground-wood pulp.

**Ash.**—Shall not exceed 10 per cent.

**Colour, Finish, Formation and Opacity.**—Deliveries must conform to standard sample.

#### ERRATA IN VOL. I.

Page 471, Fig. 76 title should read "Mullen's" instead of "Muller's."

Page 476, line 23 should read "or" instead of "of."

# ALIPHATIC ACIDS.

By ARTHUR W. THOMAS AND W. A. DAVIS.

## ACETIC ACID AND VINEGAR.

### Acetic Acid.

**Physical Properties.**—According to Bousfield and Lowry<sup>1</sup> acetic acid is best purified by distilling from potassium permanganate, using a still head to retain the acids of higher boiling point, and then freezing to remove the water. The purified acid melts at  $16.60^{\circ}$  and has a sp. gr. 1.05148 at  $18^{\circ}/4^{\circ}$  and 1.04922 at  $20^{\circ}/4^{\circ}$ ; its maximum conductivity when mixed with water is  $\kappa_{18} = 0.0016415$ . The boiling point of the pure acid is  $117.88^{\circ} \pm 0.05^{\circ}$  under 760 mm.<sup>2</sup>

According to Orton, Edwards and King<sup>3</sup> the degree of freedom of acetic acid from impurities is best judged by determining the fall in titre of a solution of bromine in the acetic acid diluted with an equal volume of water. For this purpose a standard solution of bromine (about  $N/5$ ) is made in pure acetic acid; 5 c.c. of this solution are added to 45 c.c. of the acetic acid to be tested and 50 c.c. of water are introduced. The mixture is placed *in the dark* in a bath at  $16^{\circ}$  and the free bromine determined at intervals with hydriodic acid and  $N/50$  thiosulphate.

**Impurities.**—For the *detection and estimation of acetic anhydride* when present in acetic acid in small quantities Edwards and Orton<sup>4</sup> make use of the fact that 2:4 dichloroaniline combines rapidly with acetic anhydride but not with acetic acid at the ordinary temperature. The resulting anilide is readily and quantitatively converted into a chloroamine and the accurate estimation of the latter is extremely easy owing to its quantitatively liberating iodine from hydriodic acid, the iodine being determined as usual by means of thio-sulphate.

The process is as follows: 2 gramm. of 2:4-dichloroaniline (or a quantity equivalent to about 3 times the amount of the acetic anhydride supposed to be present) is added to 100 c.c. of the acetic acid to be tested. The mixture is left overnight in a bath at  $16^{\circ}$ .

The mixture is then diluted with water so as to contain about 20% of

<sup>1</sup> *Trans.*, 1911, 99, 1432.

<sup>2</sup> Ordinary acetic acid contains traces of glyoxylic acid and hence gives the Adamkiewics reaction (Hopkins and Cole, *Proc. Roy. Soc.*, 1901, 68, 21); the acid purified in the manner described above is stable to bromine and does not give the Adamkiewics indication. Deterioration of such acid does not occur even when the acid is exposed to light or atmospheric oxidation.

<sup>3</sup> *Trans.*, 1911, 99, 1178.

<sup>4</sup> *Trans.*, 1911, 99, 1181.

acetic acid and the aniline (partly) and the anilide (wholly) extracted with chloroform. For each 100 c.c. of the diluted liquid first 10 c.c., secondly 7 c.c. and lastly 5 c.c. of chloroform are used. The unchanged aniline is now withdrawn from the chloroform by shaking for a few minutes with 10% hydrochloric acid, 160–200 c.c. being used for each gram of the aniline originally present. The chloroform is carefully drawn off in a separating funnel and the hydrochloric acid washed twice with 1 c.c. of chloroform. The chloroform solution is now mixed with an equal volume of pure acetic acid and dilute bleaching powder solution slowly added (3 to 5 times that required to convert the anilide to chloroamine). The volume of the bleaching powder solution should be equal to the volume of the glacial acetic acid, that is the acetic acid is diluted to 50%, a concentration at which the formation of chloroamine is complete. An  $N/20$  bleaching powder solution is now added in sufficient quantity to dilute the aqueous acetic acid to 20% acetic acid. For example if 30 c.c. of glacial acetic acid were added to the chloroform solution of the anilide, then 30 c.c. of bleaching powder solution would be required for the first addition and 90 c.c. of  $N/20$  bleaching powder for the second. Chloroform withdraws the chloroamine completely from 20% acetic acid. Any marked development of red colour at this stage shows that the aniline has not been properly separated.

The chloroform is drawn off into 30 to 40 c.c. of  $N/20$  bleaching powder solution, with which it is shaken to free it from acetic acid. Finally the chloroform is evaporated in a current of pure dust-free air at a temperature not exceeding  $25^{\circ}$ . The residue is dissolved in chloroform (5–10 c.c.) and treated with 5% potassium iodide and a little acetic acid; the iodine liberated is titrated with  $N/20$  thiosulphate.

**Formic Acid in Acetic Acid.**—Ost and Klein in 1908 pointed out that commercial acetic acids usually contain formic acid, different samples showing various proportions up to 0.6%, and Pikos showed that it was quite easy commercially to produce acetic acid free from this impurity. In spite of this Fincke<sup>1</sup> states that formic acid is still an impurity which is usually present (0.018 to 0.806%) in the acid used for pharmaceutical purposes. To *estimate the formic acid* present, Fincke operates as follows: 5 c.c. of the glacial acid, 5 grm. of sodium acetate, 40 c.c. of 1 in. 20 solution of mercuric chloride and 30 c.c. of water are heated in an Erlenmeyer flask fitted with a reflux condenser for 2 hours in a water-bath, the part of the flask containing the liquid being fully immersed. The precipitated calomel is collected in a Gooch crucible, dried and weighed; its weight multiplied by 0.0977 gives the weight of formic acid.

**Aluminium Acetate.**—Enz<sup>2</sup> states that a supply of dilute acetic acid (sp. gr. 1.041) used in the preparation of pharmaceutical products contained 0.095% of alumina in the form of aluminium acetate.

<sup>1</sup> *Apoth. Zeit.*, 1910, 727.

<sup>2</sup> *Apoth. Zeit.*, 1912, 27, 942.

According to the new British Pharmacopœa (1914) the following are the requirements for acetic acid (glacial). It crystallises when sufficiently cooled and does not entirely remelt until the temperature rises above  $14.7^{\circ}$ . 1 grm. diluted with 50 c.c. of water requires for neutralisation not less than 32.9 c.c. of  $N/2$  solution of sodium hydroxide. It leaves no residue on evaporation and yields no characteristic reaction for lead, copper, arsenic, chlorides, nitrates, sulphates or sulphites. It does not immediately darken in colour when neutralised with *solution of ammonia* and warmed with *solution of silver nitrate* (absence of formates). 2 c.c. of glacial acetic acid do not completely decolourise a mixture of 3 drops of *solution of potassium permanganate* and 10 c.c. of water within half a minute (limit of empyreumatic matter.)

### Vinegar.

Russell and Hodgson<sup>1</sup> give the following analyses of 12 samples of genuine malt vinegar and 2 samples of wood vinegar.

	Malt vinegars		Wood vinegars	
	Lowest	Highest	1	2
Sp. gr.....	1013.7	1022.1	1012.1	1012.4
Acetic acid, %.....	3.85	6.36	2.20	2.30
Total solids, %.....	1.47	3.15	0.47	0.43
Ash, %.....	0.18	0.60	0.04	0.03
Alkalinity of ash (as $K_2O$ % ).....	0.016	0.040	0.014	0.022
$P_2O_5$ , %.....	0.047	0.092	Nil.	Nil.

In estimating total solids it was found that the residues retained from 0.15 to 0.22% of acetic acid and that a neutral residue was obtained only when the latter was moistened with water and evaporated 3 times in succession. It is suggested that 3.5% of acetic acid and 0.05% of phosphoric acid should be taken as the standards for malt vinegar.

**Volatile Acids in Wines and Vinegars.**—Gore<sup>2</sup> describes the apparatus shown in Fig. 4 for the estimation of volatile acids in wines and vinegars. The apparatus is a modification of that due to Hortvet-Sellier, in which a copper flask is substituted for the outer glass flask and a constant-feed device for the flask has been added. A small ridge is also blown in the inner flask to form a shoulder for the rubber gasket and the dropping funnel has been eliminated as unnecessary. The constant water feed is operated by running the supply water through tube *a*, which passes through tube *b*. The overflow passes through *b* and rises through *c* to the small basin *d* which is connected to the drain. Distilled water should be used which has been largely freed from carbon dioxide by passing a rapid stream of air through it for 20–30 minutes. The rate of flow of the water is regulated by comparing the rate of

<sup>1</sup> *Analyst*, 1910, 35, 346.

<sup>2</sup> *U. S. Bureau of Chem.*, 1909, Circular No. 44.



drip in the small sight-tube *e* with that from the condenser. Experiments with the apparatus showed that when tap-water was supplied to the generator there was an error, due to the presence of carbon dioxide in the distillate equal to about 0.3 c.c. of  $N/10$  alkali in 100 c.c., when phenolphthalein was used as indicator. When ordinary distilled water was used the error was 0.15 c.c., and when the carbon dioxide was removed by aeration, as de-

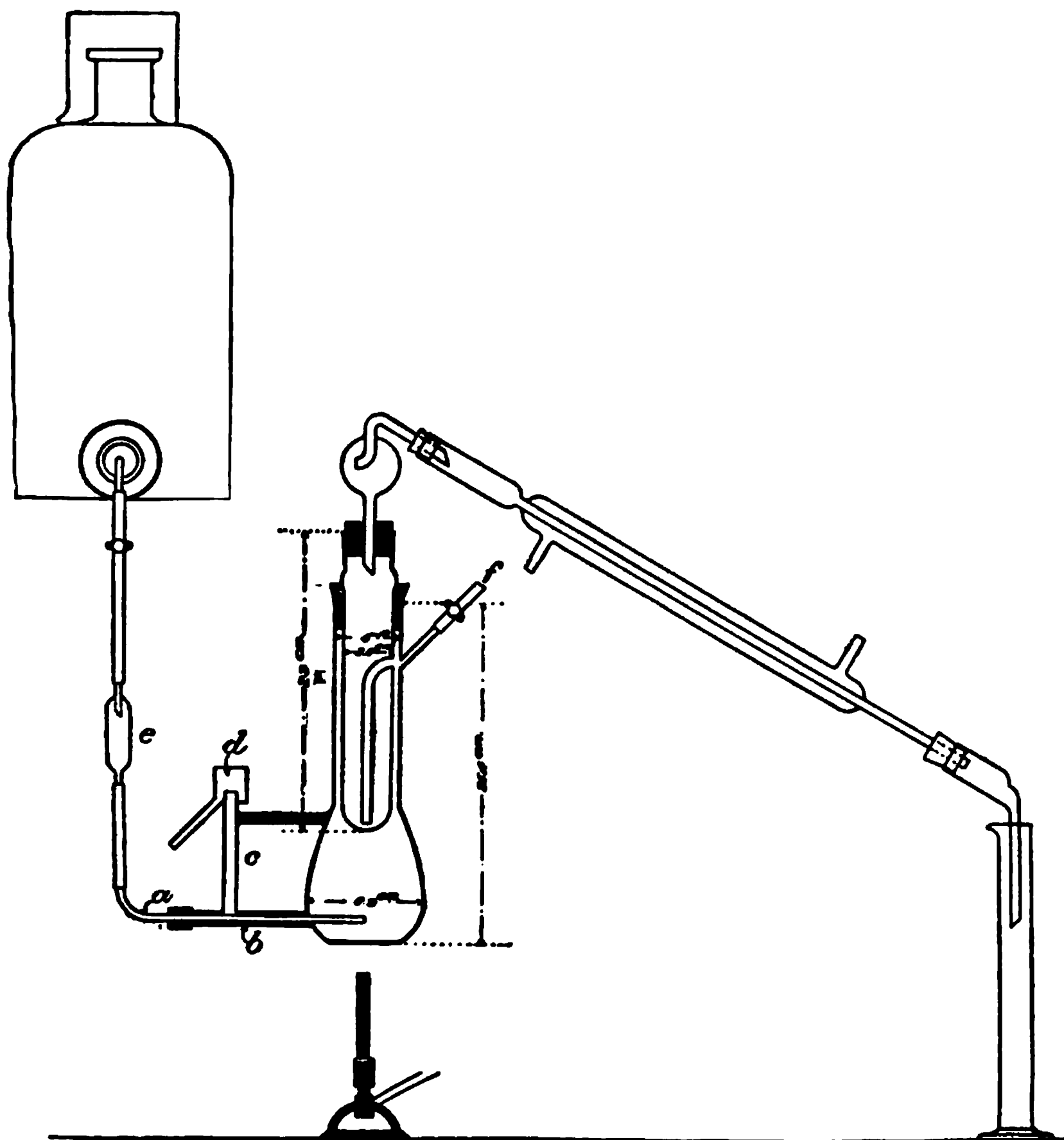


FIG. 4.—Modified Hortvet-Sellier apparatus.

scribed, the error was only 0.05 c.c. This error is constant and may be subtracted from the results. The operation is carried out as follows: 10 c.c. of the sample is placed in the inner flask which should be removed from the outer flask and be quite cool. If the sample is noticeably charged with carbon dioxide, this should be removed by passing a current of air through it, by attaching to the flask a stopper fitted with a glass tube connected with suction. The air passes in through the side tube of the flask and washes out the



carbon dioxide without removing appreciable quantities of volatile acids. The flask is then connected with the distilling bulb, and placed in the outer flask, tube *f* of the latter being open, all connections are made tight and the tube *f* is then closed. In the case of wines about 100 c.c. of the distillate are collected, in the case of vinegars 200 to 300 c.c. The distillate is titrated with standard alkali, free from carbonate, using phenolphthalein as indicator, and 0.05 c.c. is subtracted from the number of c.c. of  $N/10$  alkali used for each 100 c.c. of distillate. About 15 minutes are required for the estimation of volatile acid in wine, and from 30 to 45 minutes in the case of vinegar. The volume of liquid in the inner flask increases but slightly during the determination.

**Mineral Acids.**—According to Repiton<sup>1</sup> a portion of the sample is titrated with a solution of calcium saccharate, using phenolphthalein as indicator, to ascertain the total acidity. Another portion is neutralised with sodium hydroxide, free from carbonate, then acidified with phosphoric acid and subjected to distillation until the distillate is no longer acid. The distillate is then titrated with calcium saccharate; if the result obtained is identical with the total acidity, free mineral acids are probably not present. If there be a difference, sulphuric acid and hydrochloric acid should be determined in the ordinary way. Nitric acid is not likely to be present. Phosphoric acid is estimated by treating a portion of the vinegar with calcium carbonate, evaporating to dryness, incinerating and precipitating the nitric acid solution of the ash in the usual manner.

**Wine Vinegar.**—Fleury<sup>2</sup> states that as inositol is not decomposed during the acetous fermentation, its presence can be used as a test for the genuineness of wine vinegars, which always give a decided reaction of inositol. 100 c.c. of the vinegar are evaporated nearly to dryness, the residue is taken up with 50 c.c. of water, neutralised with sodium hydroxide and triturated with 3 gm. of barium hydroxide. The liquid is separated and the precipitate washed with 20–30 c.c. of baryta water. The liquid and washings are freed from barium by means of carbon dioxide or sulphuric acid and the defecation is completed by adding 10 c.c. of normal lead acetate solution (1:3). The clear liquid is made up to 100 c.c. and 10 c.c. of official basic lead acetate and a solution of 2 gm. of neutral cadmium nitrate added. The precipitate, which contains the inositol, is decomposed with hydrogen sulphide and the filtrate evaporated to a syrup. The residue is taken up with 20 c.c. of absolute alcohol and 5 c.c. of dry ether added. After 1 or 2 days' standing, the solution is tested for inositol by the usual methods.

**Cider Vinegar.**—From a study of fine cider vinegars F. E. Mott<sup>3</sup> concludes that there is a relation between the contents of lævulose and of dextrose therein. If the amounts of lævulose and dextrose (percentage of total solids) be plotted on squared paper as abscissæ and ordinates respectively, then a line

<sup>1</sup> *Monit. Scient.*, 1909, 23, 172.

<sup>2</sup> *J. Pharm. Chim.*, 1910, 2, 264.

<sup>3</sup> *J. Ind. Eng. Chem.*, 1911, 3, 747.

drawn from the zero point through the point corresponding to 15% dextrose and 25% of lævulose will represent the maximum values for dextrose in relation to the corresponding values for lævulose in fine cider vinegar, and a higher value for dextrose indicates adulteration with a foreign dextro-rotatory substance.

In estimating the lævulose and dextrose the following method is recommended: The total solids from 10 c.c. of the vinegar are dissolved in 25 c.c. of water, the solution made up to 100 c.c. and the reducing sugars estimated by Munson and Walker's method (see page 28). 50 c.c. of the vinegar are then treated with 5 c.c. of basic lead acetate solution and two teaspoonfuls of animal charcoal, filtered and the filtrate polarised in a 200 mm. tube at 20°. From the polarisation ( $p$ ) expressed in Ventzke degrees and the percentage of reducing sugars ( $R$ ) in the total solids, expressed as dextrose, the percentage of lævulose ( $L$ ) and of dextrose ( $D$ ) are calculated by means of the formulæ.

$$P = \frac{P \times 26.048}{\text{total solids}}; \quad L = \frac{0.793 R - P}{2.08}; \quad D = R - 0.915L$$

Mott claims that pure cider vinegar contains about 0.6 as much dextrose as lævulose, consequently if a suspected sample shows a dextrorotation of polarised light at 87° it may be adulterated with dextrorotatory substances, usually glucose. On the other hand, a lævorotation at 87° is not conclusive evidence of purity. Mott estimates the reducing sugars by the polarimeter and by Munson and Walker's method after evaporation to remove aldehydes.

**Adulteration of Cider Vinegar with Distilled Vinegar.**—Pure cider vinegars contain volatile constituents which have a reducing action on Fehling's solution. These bodies are not present in distilled vinegar or pyroligneous acid. A method based on this fact is given by S. L. Crawford<sup>1</sup> as follows: 50 c.c. of the sample are diluted to 250 c.c., placed in a distilling flask, and 200 c.c. are distilled into a 250 c.c. flask. The distillate is then neutralised, made up to 250 c.c. and 50 c.c. are taken for estimation of the reducing substances by Munson and Walker's method. Calculated to the basis of a vinegar containing 4% acid, the distillate should contain from 0.11% to 0.15% of reducing substances calculated as invert sugar. Pure cider vinegars usually contain 0.007 gm. of formic acid per 100 c.c. Pyroligneous acid would raise this figure while distilled vinegar would lower it.

**Lead Number.**—The qualitative detection of adulteration of cider vinegar by measurement of the precipitate formed by lead acetate is regarded by many to be one of the most useful of tests. For this purpose a rapid process is given by Hortvet<sup>2</sup> as follows:

To 25 c.c. of the vinegar are added 2.5 c.c. of U.S.P. lead subacetate solution. The mixture is shaken and whirled in a graduated Hortvet tube in a centrifugal machine. The volume of the precipitate in the bottom of the tube

<sup>1</sup> *J. Ind. Eng. Chem.*, 1913, 5, 845.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1904, 26, 1532.

is then read off and this volume in c.c. is termed the *Hortvet lead number*. The lead numbers of pure cider vinegars have been found to range from 0.5 to 1.4 while adulterated cider vinegars give numbers from almost zero to 0.5, rarely more than 0.5.

The Hortvet tube is 15.3 cm. in length, and consists of a wide cylindrical portion 3 cm. in diameter, narrowed at the top to a neck which is 2 cm. in diameter, and at the bottom to a stem graduated in tenths to 5 c.c. Hortvet's centrifugal machine had a radius of 18.5 cm. and was run at a speed of 1600 r.p.m.

Winton's method<sup>1</sup> of estimating the lead number of vinegars has the advantage of not requiring the use of a centrifugal machine. This method gives most satisfactory results but requires much more time than the Hortvet process, owing to the fact that the lead is estimated by a gravimetric method. Cider vinegars give Winton numbers of 0.075 to 0.290; malt vinegars much higher values, whilst distilled vinegars give much lower figures.

**Caramel in Vinegar.**—L. Ronnet<sup>2</sup> gives the following method to detect caramel in vinegar. 50 c.c. of the vinegar are mixed with an excess of calcium carbonate and evaporated to dryness. The mass is extracted with 20 c.c. of ether, the ethereal solution is filtered and the filtrate received in a test-tube containing 10 c.c. of resorcinol reagent (1 gram. of resorcinol dissolved in 100 c.c. of hydrochloric acid of sp. gr. 1.125). If caramel is present in the vinegar a red zone is formed at the junction of the two liquids. Methods which depend on heating the vinegar with albumin and extracting the evaporated solution with ether are untrustworthy as traces of furfural compounds (on which the colouration with the resorcinol reagent depends) may be formed during the evaporation, should the vinegar contain sugars.

Miss A. Anderson<sup>3</sup> obtained positive tests for furfural by the aniline acetate method in 19 out of 28 samples of *pure* cider vinegar. She also obtained indications of caramel by using Fiehe's resorcinol reagent when no caramel had been added. Hence caution must be exercised in the interpretation of results. These observations emphasise the necessity of modifying the test in some such manner as suggested by Ronnet, owing to the production of furfural derivatives from sugars (compare page 64).

### Pyroligneous Acid.

Samples of crude pyroligneous acid containing respectively 8.4 and 8.7% of acid calculated as acetic acid, were found by G. Frerichs<sup>4</sup> to give distillates containing only 3.9 and 4.2% of acetic acid. From a comparison with older samples it is concluded that crude pyroligneous acid as now sold contains acids other than acetic acid and is of inferior quality to that obtained from-

<sup>1</sup> *J. Amer. Chem. Soc.*, 1906, 28, 1204.

<sup>2</sup> *Ann. Falsif.*, 1912, 5, 517.

<sup>3</sup> *J. Ind. Eng. Chem.*, 1914, 6, 214.

<sup>4</sup> *Apoth. Zeit.*, 1913, 28, 525.

erly or may consist of a waste product from which much of the acetic acid has already been distilled.

### Formic Acid.

In testing for formic acid in distillates it must be borne in mind that the distillation of sugars with acids produces formic acid.

It is also dangerous to apply either the silver nitrate or mercuric chloride tests for formic acid to distillates, inasmuch as other volatile substances will give a positive indication with these reagents. Consequently it is advisable to convert the formic acid into formaldehyde by means of magnesium and sulphuric acid and then apply a convenient test for formaldehyde.

### Oxalic Acid.

J. M. Albahary<sup>1</sup> proposes a new method of estimating *oxalic acid* in cocoa and chocolate which gives more satisfactory results than other existing processes and is also applicable in the analysis of plant juices. It is based on the fact that magnesium salts precipitate phosphates and purine bases in alkaline solution whilst oxalates remain dissolved as magnesium alkali oxalates.

The procedure is as follows:

50 grm. of the sample are dried over sulphuric acid to constant weight and then heated on a water-bath for 1 hour with 50 c.c. of 10% sodium carbonate solution, the volume being kept constant during the heating by adding water from time to time. The mixture is then treated with 50 c.c. of a solution containing 10% of magnesium chloride and 20% of ammonium chloride, a quantity of animal charcoal being added to retain mucilaginous substances. After concentrating by heating for 1 hour, with occasional shaking, the mixture is filtered hot by means of suction, and the residue washed with boiling water. The filtrate is concentrated, made strongly alkaline with ammonia and after standing 12 hours is filtered. The filtrate is treated with a slight excess of calcium chloride and made faintly acid with acetic acid. After standing 12 hours the calcium oxalate is filtered off and the oxalic acid determined in the usual way. This gives total oxalates. If the preliminary treatment with sodium carbonate be omitted, the final result will give soluble oxalates and the difference between the two results gives the amount of calcium oxalate present.

### Succinic Acid.

After a critical study of all the existing methods for the estimation of *succinic acid in wine*, C. von der Heide and H. Steiner<sup>2</sup> recommend that the following method be used when accurate results are desired:

<sup>1</sup> *J. Soc. Chem. Ind.*, 1909, 28, 738.

<sup>2</sup> *Zeit. Unters. Nahr. Genussm.*, 1909, 17, 291. *Zeit. Anal. Chem.*, 1912, 51, 628.

50 c.c. of wine are evaporated in a 200 c.c. casserole to remove all alcohol. After adding 1 c.c. of 10% barium chloride solution and phenolphthalein the solution is neutralised with powdered barium hydroxide, the excess of barium is removed by means of carbon dioxide and then 85 c.c. of 95% alcohol are added to the mixture whilst constantly stirring. After 2 hours the precipitate of barium succinate, tartrate, malate and other barium salts is collected on a filter, washed with a small quantity of 80% alcohol and then washed back into the casserole with hot water. The solution is concentrated to remove all alcohol, 5% potassium permanganate solution is then added in 3 c.c. portions until the red colour persists for 5 minutes. An additional 5 c.c. of permanganate is added and the mixture heated on a water-bath for 15 minutes. The excess of permanganate is reduced with sulphurous acid and after acidifying with sulphuric acid more sulphurous acid is added until the manganese dioxide is dissolved. The mixture is then evaporated to about 30 c.c. and after acidifying with sulphuric acid until about 10% of free acid is present is extracted with ether for 12 hours in a percolating apparatus. The ethereal solution is evaporated with water and the residual aqueous solution is made alkaline with barium hydroxide. The mixture is then heated on a water-bath for 10 minutes, excess of barium is precipitated as carbonate, and the solution cooled and filtered. 20 c.c. of *N*/10 silver nitrate are added to the solution in a 100 c.c. flask and diluted to the mark. After standing 2 hours the excess of silver in a 50 c.c. portion is titrated by the Volhard method.

### Malic Acid.

**Estimation of Malic Acid.**—A method of estimating malic acid in fruit juices is described by P. B. Dunbar and R. F. Bacon.<sup>1</sup> This method has been supplemented by D. S. Pratt<sup>2</sup> with a preliminary treatment which removes several mechanical difficulties in the original process. The modified method is carried out as follows:

A weighed amount of juice, generally 100 gm., is placed in a 500 c.c. beaker. With vigorous stirring about 2 or 3 times the volume of 95% alcohol is added. This throws out the pectin bodies, usually in such a form that after standing a few minutes they may be gathered into a coherent mass. The liquid is decanted through a filter and the precipitate washed twice with 95% alcohol. The combined filtrates are then evaporated in a current of air on the water-bath to about 75 c.c. After cooling, the solution is transferred to a 100 c.c. measuring flask, using 10 to 15 c.c. of 95% alcohol, sufficient sodium hydroxide is added to neutralise the solution and then the volume is adjusted to 100 c.c. The temperature when the volume is made up to the mark should be close to that at which the polarimeter readings are to be taken.

<sup>1</sup> U. S. Dept. Agr., Bur. Chem., Circular, 76. *J. Ind. Eng. Chem.*, 1911, 3, 826.

<sup>2</sup> U. S. Dept. Agr., Bur. Chem., Circular 87.

25 c.c. of this solution are treated with about 2.5 gm. of powdered uranyl acetate. In case all the uranyl acetate should dissolve in 2 hours, more should be added. This mixture is shaken vigorously at frequent intervals during the 2-hour period and then filtered through a folded filter until clear and is polarised in a 200 mm. tube against white light in a saccharimeter. If the alcohol has caused some fruit colour to pass into solution the addition of a tiny drop of bromine and vigorous shaking and filtering, if necessary, before reading will give satisfactory results. This solution and reading are designated A.

The remainder of the original filtrate is treated with powdered normal lead acetate until the precipitation is just complete. An excess of lead acetate should be avoided so as to obviate dissolution of lead malate. This mixture is cooled in an ice box and filtered until clear. The clear filtrate is then warmed to room temperature and a small crystal of lead acetate added; if no precipitate forms the excess of lead is removed by addition of anhydrous sodium sulphate. This solution is filtered until clear and polarised. This reading is designated as B. Solutions which are sufficiently clear and contain less than 10% of sugar may be polarised directly without treatment with lead acetate.

If reading B is negative, a portion of solution B is treated with uranyl acetate as described for solution A and polarised. This reading is designated as C. If B is positive, reading C need not be made.

If the solutions are too dark to be read in a 200 mm. tube, a shorter tube may be used but the observed readings should be calculated to those obtainable with a 200 mm. tube. If reading C is numerically less than reading B, the latter should be discarded, otherwise reading B should be used in subsequent calculations.

The algebraic difference between this reading and reading A multiplied by the factor 0.036 gives the percentage of malic acid.

To estimate malic acid in cane and maple products the method of P. A. Yoder<sup>1</sup> should be used.

A colour test to distinguish between *succinic* and *malic acids* is given by W. O. deConinck<sup>2</sup> as follows:

Heat a concentrated aqueous solution of the acid with calcium salicylate. Succinic acid gives a permanent rose colour which does not fade on standing in sunlight for several days. Malic acid gives a similar colour, but on 15 to 20 minutes boiling it darkens and then disappears, leaving a yellowish liquid.

### Tartaric Acid.

**Analysis of Tartaric Acid Raw Material.**—Although the analysis of raw material used in the manufacture of tartaric acid and its salts (cream of

<sup>1</sup> *J. Ind. Eng. Chem.*, 1911, 3, 563.

<sup>2</sup> *Bull. Soc. Chem.*, 1914, 15, 93.



tartar, Rochelle salt, tartar emetic) is now generally made by the "Goldenberg 1907 Method" (Vol. I, page 545) during the past 2 or 3 years the so-called "London Method" has been adopted for purposes of sale of tartars (argols, vinaccia tartar) and tartrate of lime in the London market; lees are still purchased in the London market on analyses made by the Goldenberg method.

**London Method for Argols and Similar Tartars (Alambic Tartars).—**1.5 gm. of the finely divided sample are washed into a 350 c.c. beaker (tall form) with 10 c.c. of a solution of potassium carbonate (40 gm.  $K_2CO_3$  in 100 c.c. of water); about 2 gm. of purified animal charcoal and water to make about 25 c.c. in all are added. The mixture is boiled gently for 20 minutes. The solution is then filtered by means of a vacuum apparatus, into a 550 c.c. beaker (tall form), the residue being washed with hot water until a total volume of 150 c.c. is obtained. 5 c.c. of hydrochloric acid (sp. gr. 1.1) are added and the solution concentrated to about 15 c.c. on a hot plate, avoiding actual ebullition. 4 c.c. of glacial acetic acid are then added and the mixture well stirred for 5 minutes. When the mixture is cold, 100 c.c. of 92 to 95% alcohol are added and the mixture is again stirred for 5 minutes. After the precipitated potassium hydrogen tartrate has stood for  $\frac{1}{2}$  hour, it is filtered off on a filter-pump plate and washed with alcohol, exactly as in the Goldenberg method, until the washings are free from acidity (see Vol. I, page 546). The precipitate is dissolved in 200 c.c. of hot water and the solution is titrated, whilst boiling, with  $N/5$  sodium hydroxide.

Phenolphthaleïn is used as indicator, and as the solutions are frequently highly coloured, it is used as an outside indicator on a clean white glazed tile. The sodium hydroxide used should be standardised with pure dry recrystallised potassium hydrogen tartrate under similar conditions.

For tartrate of lime the same method is employed but the animal charcoal can be omitted.

**London Method for Vinaccia and High-grade Tartars.**

**1. Tartaric Acid Present as Bitartrate.—**5 gm. of the sample are washed into a 400 c.c. beaker with 250 c.c. of hot water and 15 c.c. of  $N$ -sodium hydroxide. After boiling for 10 minutes, the titration is completed with  $N$ -sodium hydroxide using phenolphthaleïn as indicator.

**2. Tartaric Acid Present as "Tartrate of Lime" (Calcium Tartrate).—**2 gm. of the sample are ignited in a covered platinum dish or crucible at a low temperature. When charred, the residue is washed into a beaker with 5 c.c. of hydrogen peroxide (10 volume), 30 c.c. of normal hydrochloric acid are added and the solution well boiled to destroy the excess of peroxide. Phenolphthaleïn is then added and the solution titrated back with  $N$ -sodium hydroxide. In this way the number of c.c. of  $N$ -HCl required to neutralise the ash of 1 gm. is obtained. From this is deducted the number of c.c. of  $N$ -sodium hydroxide required to neutralise the bitartrate present in 1 gm., as found by method 1, and the percentage of tartaric acid in the form of calcium

tartrate is calculated from the difference (each c.c. = 0.075 grm. of tartaric acid in the form of calcium tartrate).

**Control of Working Conditions in Tartaric Acid Factories.**—For the methods of analysis used in the control of factory operations during the manufacture of tartaric acid reference should be made to Lunge-Keane's "*Technical Methods of Chemical Analysis*," Vol. 3.

### Commercial Tartaric Acid.

The following summary of the tests for *ash*, *arsenic* and *lead* is taken from the article on tartaric acid in Lunge-Keane's "*Technical Methods of Chemical Analysis*," Vol. 3.

**Ash.**—The limit for ash in tartaric acid crystal or powder used for pharmaceutical purposes in Great Britain in past years has been 0.05%. The Committee of Reference to the Pharmacopœia Committee (1908) (see British Pharmacopœia, 1914) has, however, recommended that this limit should be raised to 0.1%.

**Arsenic** is tested for by the following method recommended by the Royal Commission on arsenical poisoning (1903). From 1–5 grm. of tartaric acid are used, with arsenic-free zinc and hydrochloric acid. The limit of arsenic adopted is 1/100 grain per pound (1.4 parts  $\text{As}_2\text{O}_3$  per million, or 0.00014%). There is no difficulty in obtaining tartaric acid in which arsenic falls considerably below this figure.<sup>1</sup>

**Lead.**—The limit of lead generally adopted in commerce in Great Britain is 20 parts per million (0.002%), as recommended by McFadden.<sup>2</sup> Many methods have been suggested for making the test, of which the following are probably the most reliable:

**Method I.**—Based on C. A. Hill's method,<sup>3</sup> which is, like the following one, a modification of Warrington's original colourimetric method.<sup>4</sup> Hill's process has been adopted by the 1914 British Pharmacopœia, and is described therein in detail.

A standard lead solution is prepared containing 5 parts of lead per million, by dissolving pure metallic lead in a minimum quantity of nitric acid (equal parts of concentrated acid and water) and suitably diluting; it is best to prepare a standard stock solution of lead, containing say 1 grm. of lead per litre, and then, when required, to dilute this for use to the above concentration. The standard solution may also be prepared from pure lead nitrate or from crystalline lead acetate.

For the test, 7 grm. of the sample are weighed out, and a separate portion of 2 grm. for the colourimetric comparison. Each portion is dissolved in about 10–15 c.c. of water, and to the 2 grm. portion are added as many c.c. of the standard lead solution as there are suspected to be parts per million of

<sup>1</sup> Cf. A. W. McFadden, Local Government Board Report, Inspector of Foods, No. 2, 1907.

<sup>2</sup> Cf. Tatlock and Thomson, *Analyst*, 1908, 33, 173; T. P. Harvey and J. M. Wilkie, *Chem. and Drug.*, 1909, 75, 92.

<sup>3</sup> *Chem. and Drug.*, 1905, p. 388.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1893, 12, 97.



lead in the tartaric acid tested. Thus to compare with 15 parts of lead per million, 15 c.c. of the standard lead solution are used. To each solution are then added 1–2 c.c. of 10% potassium cyanide solution and 13 c.c. of ammonia of sp. gr. 0.880, and the solutions are boiled for half a minute or longer so as to get both colourless if possible. They are next poured into two 50 c.c. Nessler cylinders of clear white glass and diluted to an equal volume (50 c.c.), any difference of colour being corrected if necessary by the addition of a drop or two of a very dilute solution of caramel. To each solution are then added 1–2 drops of a freshly prepared colourless ammonium sulphide solution (obtained by saturating ammonia (sp. gr. 0.880), diluted with an equal volume of water, with hydrogen sulphide gas, carefully washed by passing through water). The colour of the two solutions is compared by examining them, placed on a sheet of white paper, in a good light.

Generally it is sufficient to make sure that the quantity of lead present is less than 20 parts per million, but if it is necessary to ascertain the exact quantity, comparisons are made with suitable proportions of lead (5, 10, 15, etc., c.c. of the dilute standard lead solution).

*Method II.—J. M. Wilkie's Method.*<sup>1</sup>—7 gm. of the sample are taken for the test, and 2 gm. for the colourimetric comparison, to which the standard lead solution is added. Each is dissolved in about 35 c.c. of hot water, allowed to cool, a few drops of *N*/10 sodium thiosulphate solution added, and heated to incipient boiling, when the flame is removed. Any ferric iron present is rapidly reduced on cooling. When the solution is water-white, potassium cyanide (1–2 c.c. of 10% solution) is added, and then ammonia until the solution just smells of it (excess should be avoided). After diluting in Nessler cylinders, 2 drops of colourless ammonium sulphide solution are added and the colourations compared as described above.

In Germany, the following test, due to W. Klapproth, is used. 20 gm. of the sample are ignited with 0.04 gm. of calcium carbonate in a porcelain crucible. The small residue (which contains all the lead) is dissolved in a few drops of nitric acid, 2 or 3 drops of sulphuric acid added, and the mixture heated to expel the nitric acid. The residue, consisting of lead and calcium sulphates, is dissolved in ammonium acetate solution and the solution filtered from insoluble matter (ferric oxide).

To the clear solution hydrogen sulphide water is added and the resulting brown colouration compared with that of a solution of ammonium acetate in water, containing a known quantity of lead to which hydrogen sulphide water has been added under similar conditions. To make certain that the brown colouration is due to lead and not to copper, some potassium cyanide solution is added, which destroys the brown colour due to copper, but has no effect on that due to lead.

**Other Tests.**—Quantities of 3 gm. of the acid are dissolved in water and submitted to the following tests.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1908, 28, 636; Harvey and Wilkie, *Chem. and Drug.*, July 17, 1909.

The solution of the pure acid should give no turbidity with barium chloride; nor, after the addition of nitric acid, with silver nitrate. The solution rendered alkaline with ammonia should give no precipitate with ammonium oxalate. The acid should require for titration the calculated quantity of normal alkali, which has been standardised by pure potassium hydrogen tartrate, using phenolphthaleïn as indicator, under exactly the same conditions of concentration.

**British Pharmacopœia, 1914.**—The requirements of the new Pharmacopœia are as follows for tartaric acid: 1 grm. dissolved in water requires for neutralisation not less than 13.2 c.c. of *N*/1 solution of sodium hydroxide. Yields no characteristic reaction for copper, iron, or oxalates and not more than the slightest reaction for calcium. *Lead limit* 20 parts per million; *arsenic limit* 1.4 parts per million. 1 grm. dissolved in 50 c.c. of water on addition of 0.5 c.c. of *solution of barium chloride* does not yield a greater opalescence than 1 c.c. of *N*/100 solution of sulphuric acid when precipitated under the same conditions (limit of sulphates); ash not more than 0.1%.

**Cream of Tartar.**—This occurs in commerce in different grades of purity, containing varying proportions of calcium tartrate or calcium sulphate. The usual qualities are 95, 98, and 99–100%.

The total tartaric acid is best estimated by the Goldenberg method.

The *acidity*, on which the percentage of cream of tartar is generally gauged, is ascertained by titrating 5 grm. of the sample with *N*/1 potassium hydroxide, which has been standardised by titration with 5 grm. of pure recrystallised 100% cream of tartar, dried at 100°, under exactly the same conditions of concentration, using phenolphthaleïn as indicator. The titration can also be made with 2 grm. of the cream of tartar and *N*/5 alkali standardised under the same conditions as in the actual test. The observance of exactly similar concentrations for standardisation and the actual test is necessary if exact results are to be obtained, owing to the hydrolysis of the neutral tartrate by water, which causes more alkali to be required (0.1–0.3 c.c.) in dilute solution than in concentrated solution.

To estimate tartaric acid rapidly in cream of tartar, baking-powders, etc., F. W. Richardson and J. C. Gregory.<sup>1</sup> and R. O. Brooks<sup>2</sup> have advocated a polarimetric method.

The requirements as regards *arsenic* and *lead* are the same as for tartaric acid.

**Other Methods of Estimating Tartaric Acid.**—It is generally recognised that the Goldenberg method, using litmus as indicator, gives slightly low results for tartaric acid when, as is usual in the case of raw material such as lees and crude tartars, phosphates of aluminium and iron are present or certain other substances such as malic acid or gummy impurities accompany

<sup>1</sup> *J. Soc. Chem. Ind.*, 1903, 22, 405.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1904, 26, 813.

the tartaric acid.<sup>1</sup> As, however, the presence of such impurities in tartaric acid raw material causes considerable loss of the acid during its manufacture, the Goldenberg method represents, in the case of the lower grade material probably the fairest means of arriving at the value of such consignments. It must be remembered, however, that the Goldenberg process is a conventional one, and may, when absolute results are required, give rise, in presence of the impurities enumerated above to some considerable degree of error, ranging from 0.5 to 5% of the tartaric acid present, according to the proportion and nature of the impurities present.

Various other processes of estimating tartaric acid have therefore been suggested, none of which has yet been adopted for commercial purposes. A brief description of some of the most promising of these methods is here appended, as in certain special cases such methods might find a useful application.

**Chapman and Whitteridge's Method.**<sup>2</sup>—In this method, the tartaric acid is precipitated from its solution as bismuth tartrate, the latter being practically insoluble in dilute acetic acid; the barium tartrate is titrated, subsequently, in sulphuric acid solution, with potassium permanganate. The process is carried out as follows: A known weight of the substance to be analysed, containing about 0.1 gm. of tartaric acid, is dissolved in 40 c.c. of water; the solution is neutralised with either sodium hydroxide or acetic acid, as the case may require, and is then heated nearly to boiling. 15 c.c. of bismuth reagent (prepared by dissolving 30 gm. of crystallised bismuth nitrate in 20 c.c. of glacial acetic acid, diluting the solution to a volume of 300 c.c. with water, and filtering, if necessary) are added, the mixture is stirred vigorously for a few minutes, and the precipitate is collected on a filter and washed well with boiling water. The precipitate is then dissolved off the paper with about 20 c.c. of hot 10% (by volume) sulphuric acid, a further 30 c.c. of the same acid being used to wash the paper. A 1% potassium permanganate solution is then run into the hot acid filtrate until a slight excess, not exceeding 0.5 c.c., is present, and this is titrated back with oxalic acid solution containing 19.9 gm. of the pure crystallised salt per litre. As the result of many determinations, it is found that 0.1 gm. of tartaric acid corresponds with 14 c.c. of the permanganate solution. For complete precipitation, it is well to add one and a half times the quantity of bismuth reagent theoretically necessary. The method gives accurate results in the case of Rochelle salt, crude tartars, Seidlitz powders, and baking powders. Alum and succinic acid, if present, have no influence on the accuracy of the results, but the method cannot be applied to the determination of tartaric acid in the presence of citric, oxalic, and malic acids.

<sup>1</sup> Compare Heczko, *Zeit. Anal. Chem.*, 1911, 50, 12. The objections which have been raised to the Goldenberg method since its adoption are based on facts which were well realised by the manufacturers and committees responsible for its acceptance as a practical test of the value of raw material on the grounds given above. The proposal by Ordonneau (*Bull. Soc. Chim.*, 1909 [iv], 7, 1034), that phenolphthalein should be used as indicator would lead to higher prices being paid for low-grade material, the tartaric acid of which cannot be completely extracted owing to the presence of alumina, phosphoric acid, etc.

<sup>2</sup> *Analyst*, 1907, 32, 163.

**Beys' Method.**<sup>1</sup>—Between 1 and 2 gram. of the material to be analysed is heated for half an hour on the water-bath with an equal weight of sulphuric acid diluted with 20 times its volume of water. When the liquid is cool, 5 times its volume of alcohol and 10 times its volume of ether are added, and the liquid filtered. The residue is washed with a mixture of 1 part of alcohol with 2 parts of ether. Some phenolphthaleïn is added to the filtrate, which is neutralised with potassium hydroxide dissolved in 90% alcohol. The amount of the latter is noted, and 5–10 c.c. more are added. The whole is heated till the ether begins to boil off, when it is allowed to cool. The clear liquid is poured off and excess of glacial acetic acid added. The crystals left behind are heated with 12–15 c.c. of water and 5 c.c. of glacial acetic acid are added, causing the precipitation of the greater portion of the potassium bitartrate. 30 c.c. of 96% alcohol are added, which is about the quantity required to make the alcoholic strength of the mixture 65%. After shaking for a few minutes and standing for an hour the precipitate is filtered off, washed first with 15 c.c. of 65% alcohol, then with 96% alcohol. The other precipitate produced by the addition of acetic acid (see above) is washed with 96% alcohol. Both precipitates are dissolved in the same quantity of boiling water. The liquid is then titrated as in the Goldenberg method, but using phenolphthaleïn as indicator.

**Kling's Method.**<sup>2</sup>—The errors which arise in the usual method of estimating tartaric acid by precipitation of its acid potassium salt are said to be avoided by precipitating the acid as calcium racemate,  $\text{Ca}(\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 8\text{H}_2\text{O}$ , and titrating a solution of this with potassium permanganate. The details of the method are as follows: 25 c.c. of a solution of *d*-tartaric acid (containing 3–4 gram. per litre) are added to 100 c.c. of water, 25 c.c. of a solution of *L*-Seignette salt (16 gram. per litre: free from *d*-salt) and 20 c.c. of a solution of pure calcium acetate (30 gram. per litre). The precipitate is collected, washed and dissolved in 20 c.c. of hydrochloric acid (40 gram. per litre). The solution is diluted to 150 c.c. and added to 40 c.c. of a solution of sodium acetate (10%) and of calcium acetate (1%) and boiled. After cooling the racemate is collected, washed with water, redissolved in 10% boiling sulphuric acid and titrated at the boiling point with a solution of permanganate (containing about 16 gram. per litre) of which the titre has been determined by means of pure bitartrate. The method gives good results and can be used for the estimation of tartaric acid in wines.

In a later paper Kling and Florentin<sup>3</sup> have modified this process so as to determine with a considerable degree of accuracy, tartaric acid contained in metallic salts, tartars, and lees.

The solutions required are: (a) A solution of di-ammonium citrate, containing 50 gram. of the salt per litre; (b) a solution containing 20 gram. of pure *L*-ammonium tartrate (free from the *d*-compound (see below, page 107),

<sup>1</sup> *Bull. Soc. Chim.*, 1910, 7, 697.

<sup>2</sup> *Compt. rend.*, 1910, 150, 616.

<sup>3</sup> *Eighth Int. Congress App. Chem.*, 1912, Sect. I, 237.

and 5 or 6 c.c. of formaldehyde (as preservative) per litre; (c) a solution prepared by dissolving 16 gm. of chemically pure calcium carbonate in 120 c.c. of glacial acetic acid and diluting to 1 litre; (d) dilute hydrochloric acid containing 40 gm. of the 22° Bé. acid per litre; (e) a solution prepared by dissolving 5 gm. of calcium carbonate in 20 gm. of acetic acid, adding 100 gm. of sodium acetate and diluting to 1 litre; (f) a solution of potassium permanganate containing 16 gm. per litre. The permanganate is standardised against a solution of tartaric acid of known titre, determined with *N/10* potassium hydroxide. In the determination of tartaric acid, in the presence of interfering metals or not, the solution is diluted to a volume of 150 c.c., 10–15 c.c. of solution *a* are added, and then successively 25 c.c. of solution *b* and 20 c.c. of solution *c*. The mixture is agitated and allowed to stand for several hours (12 hours if appreciable quantities of interfering metals are present). After being filtered off and washed with cold water, the precipitated racemate is dissolved in 20 c.c. of the dilute hydrochloric acid (solution *d*), the solution is diluted to 150 c.c., 40–50 c.c. of solution *e* are added, the mixture is heated to about 80° C. and then allowed to cool for several hours. The resulting precipitate is filtered off, washed, redissolved in hot, dilute sulphuric acid (10% by volume) and titrated at the boiling point with the permanganate solution.

This process was also applied by Kling and Gelin<sup>1</sup> to solutions prepared by heating alcoholic solutions of tartaric acid in sealed tubes and containing known amounts of tartaric acid, the latter being present in the free state and in the form of acid and neutral ethyl tartrates. The amount of tartaric acid corresponding to the total acidity being found by titration with *N/10* potassium hydroxide, the free acid present was determined by the racemate method in a second portion of the liquid. A third portion was hydrolysed with alkali in very dilute solution, the racemate process being then applied to estimate the total (free and combined) acid in the liquid. The results thus obtained were concordant and corresponded with the amounts of tartaric acid known to be present. The process is stated to be applicable to wines and other fermented liquors.

According to Kling and Florentin<sup>2</sup> the racemate method for the determination of tartaric acid was found to yield accurate results even in the case of materials containing considerable quantities of iron and aluminium oxides. The results obtained are, in certain cases, somewhat higher than those found by the usual methods, this being due to the fact that the racemate-citrate method gives the whole of the tartaric acid present.

**Estimation of Tartaric Acid in the Presence of Malic and Succinic Acids (Wines and Fruit Juices).**—The simple evaporation method proposed originally by Pasteur, and modified by Reboul, was found by Mestrezat<sup>3</sup> to give accurate results in the determination of tartaric acid in wines, and is consid-

<sup>1</sup> *Eighth Int. Congress App. Chem.*, 1912, Sect. I, i, 251.

<sup>2</sup> *Ann. Falsif.*, 1912, 5, 518.

<sup>3</sup> *Ann. Chim., Anal.*, 1908, 13, 433.



ered to be a better method than the official (French) process. The author prefers to work as follows: 50 c.c. of the wine are evaporated to the consistency of a syrup; when cold the residue should be semi-fluid, but, if the evaporation has been carried too far, a few drops of water may be added. The basin containing the residue is then placed aside for at least 4 days; after this time, the mass is taken up with a small quantity of 40% alcohol saturated with potassium bitartrate, and the solution is carefully decanted from the crystals. The latter are washed with the same solution, by decantation and then titrated. Results are given showing that concordant analyses may be made by the method and that the presence of malic, succinic and acetic acids, is without influence on the determinations.

Kling and Gobert<sup>1</sup> have applied the racemate method described above to substances which are strongly acid but contain tartaric acid in only small amount, such as vinegar, cider and perry. Fully satisfactory results were obtained, whereas those found by the methods generally used were frequently much too low. It is emphasised that in using the racemate method it is very necessary to use pure *l*-tartrate and in purifying the commercial product from the *d*-compound the following procedure has been found convenient: 20 gm. of ammonium *l*-bitartrate are dissolved in 900 c.c. of water; 20 c.c. of this are diluted to 200 c.c. with water, and to this liquid 10 c.c. of the solution of calcium acetate (*supra*) added. After half an hour, the precipitate is filtered off, washed, dried and calcined, and from the weight of residue the amount of calcium acetate which should be added to the 880 c.c. to separate all the *d*-tartaric acid, is calculated. This addition being made, the liquid is allowed to stand for 12 hours, filtered and diluted to a litre, a little formaldehyde being added as preservative. This constitutes the solution *b* (*supra*).

Gowing-Scopes<sup>2</sup> has investigated the method proposed by J. von Ferentzy,<sup>3</sup> which is based on the insolubility of basic magnesium tartrate in 50% alcohol and finds that tartaric acid may be accurately estimated in fruit juices by this method, and also in wines, if the tannic acid be first removed. More accurate results are obtained if the basic magnesium tartrate is titrated with permanganate than when it is ignited as recommended by Ferentzy. The following are the details of the process: A solution of the substance under examination, containing not less than 0.05 gm., and not more than 0.10 gm., of tartaric acid, is taken for the estimation; if the bulk of the solution be large, or if alcohol be present, the solution is evaporated to about one-half of the original volume. To the cooled solution is then added an equal volume of absolute alcohol and the precipitate which forms in the case of fruit juices and wines is filtered off and washed with 50% alcohol (by volume). 10 c.c. of ammonia and 10 c.c. of absolute alcohol are added to the filtrate, any precipitate which forms being again removed by filtration and washed with 50% alcohol. To the

<sup>1</sup> *Bull. Assoc. Chim. Suer.*, 1911, 28, 760.

<sup>2</sup> *Analyst*, 1908, 33, 315.

<sup>3</sup> *Chem.-Zeit.*, 1907, 31, 1118.

filtrate thus obtained are added 10 c.c. of "magnesia mixture" and 10 c.c. of absolute alcohol, the mixture being thoroughly stirred meanwhile. After standing overnight, the solution is filtered through double filter papers, the precipitate is washed with 50% alcohol and is then dissolved off the filter with boiling water, about 400 c.c. being used. The solution is evaporated to a volume of about 200 c.c., or until all the alcohol has been removed, then cooled and diluted to a volume of about 400 c.c., after the addition of 10 c.c. of concentrated sulphuric acid. The solution is next heated to a temperature of 90° C., and potassium permanganate solution is run in a little at a time, until 2 or 3 drops have been added in excess; this excess is then titrated back with oxalic acid solution. The potassium permanganate solution should contain 6.9745 gm. of the salt per litre; 1 c.c. corresponds with 0.0050 gm. of tartaric acid. The oxalic solution should be of equivalent strength.

The following method of estimating malic and tartaric acids in the same solution has been proposed by Dunbar:<sup>1</sup> Solutions of both malic and tartaric acids when treated with uranyl acetate show an increased rotation, which, within certain limits, is proportional to the concentration;<sup>2</sup> both acids reduce definite quantities of potassium permanganate in alkaline solution and form oxalic acid quantitatively. Hence it is possible to calculate the amounts of malic and tartaric acids in a solution, knowing the total change in the rotation on treatment with uranyl acetate, and also either the amount of potassium permanganate reduced or the amount of oxalic acid formed. The details of the method are as follows: 85 c.c. of the solution are rendered slightly alkaline with sodium hydroxide, and 5 gm. of sodium acetate are dissolved in the mixture, which is then made acid with citric acid and diluted to 100 c.c. About 30 c.c. of this solution are shaken for 3 hours with from 2 to 3 gm. of uranyl acetate; if all the latter dissolves more must be added. After filtration, the solution is polarised in a 200 mm. tube, and the reading in degrees Ventzke observed calculated to the basis of the original solution. If optically active substances other than malic and tartaric acids are present, 50 c.c. of the original solution must be treated with an excess of dry powdered lead acetate, filtered, the excess of lead removed from the filtrate by means of anhydrous sodium sulphate, and the solution polarised. The difference between the two readings will give the rotation due to the uranium complexes of the two acids. The quantity of permanganate reduced by the mixed acids is determined by rendering a portion of the solution alkaline with sodium hydroxide, adding an excess of about 3 gm. of the latter and heating the mixture with 50 c.c. of a 1.5% permanganate solution on the water-bath for 1 hour. The mixture is then acidified with sulphuric acid and the excess of permanganate titrated with oxalic acid solution. In the presence of other substances which reduce permanganate but do not form oxalic acid, the amount of the latter may be determined in the usual way by titration with permanganate; 1 c.c. of 1.5% potassium permanganate solu-

<sup>1</sup> U. S. Dept. Agric., Bureau of Chem., Circular No. 105, Oct. 4, 1912.

<sup>2</sup> See *J. Soc. Chem. Ind.*, 1911, 1177, 1407, compare p. 98.



tion is equivalent to 0.0299 grm. of crystallised oxalic acid. Let  $x$  be the grm. of malic acid, and  $y$  the grm. of tartaric acid, per 100 c.c. of solution,  $a$  the polarisation in degrees Ventzke in a 200 mm. tube after treatment with uranyl acetate, and  $b$  the grm. of potassium permanganate required to oxidise 100 c.c. of the solution, then  $x = -0.0185a + 0.1720b$ , and  $y = 0.0248a + 0.2436b$ . If  $c$  equals grm. of oxalic acid yielded by 100 c.c. of the solution then  $x = -0.020a + 0.233c$ , and  $y = 0.023a + 0.331c$ . The data taken into account in these equations are: 1 grm. of malic acid in 100 c.c. will show a rotation of  $-27.77^\circ$  V. after treatment with uranyl acetate, and 1 grm. of tartaric acid per 100 c.c. a rotation of  $19.61^\circ$  V.; 1 grm. of malic acid reduces 2.8297 grm.  $\text{KMnO}_4$  and 1 grm. of tartaric acid reduces 2.1062 grm. In the case of fruit juices and solutions containing sugars, 50 c.c. of the solution are mixed with about 150 c.c. of 95% alcohol and the mixed acids are precipitated with lead acetate; the precipitate is collected on a filter, washed with 80% alcohol until free from sugars, then decomposed with dilute sulphuric acid, the lead sulphate is removed by filtration and the alcohol by evaporation and the solution of acids so obtained treated as above described.

Another recent method<sup>1</sup> for the separate estimation of tartaric, malic and succinic acids when occurring together depends on the fact that, under certain defined conditions (faint acidity and relatively low concentration of alcohol), all three acids are precipitated by lanthanum nitrate, whereas other conditions, also closely defined, determine the precipitation of tartaric acid alone, or of tartaric and malic acids. This is the latest result of the work of Dutoit and Duboux referred to on page 13.

### Citric Acid.

**Citrate of Lime.**—The analysis of commercial calcium citrate (citrate of lime) is now generally carried out by Warington's method modified as follows:

4 grm. of the citrate are boiled with 30 c.c. of 2*N*-hydrochloric acid in a 100 c.c. standard measuring flask for 10 minutes, the solution being then cooled and made up to the mark with water. It is then shaken and filtered through a dry filter paper, 50 c.c. of the filtrate being measured by a standard pipette into a beaker of 300 c.c. capacity and exactly neutralised with dilute sodium hydroxide free from carbonate, using phenolphthaleïn as indicator. The solution is next made slightly acid by the addition of 3 or 4 drops of *N*-hydrochloric acid, 2 c.c. of a 45% solution of calcium chloride added, the liquid raised to the boil and kept boiling for 15 minutes; to avoid bumping it is necessary to stir the liquid well until actually boiling, after which it can safely be left. The hot liquid is filtered and the precipitate on the filter paper washed with boiling water 6 times. The filtrate and washings are then made just alkaline by adding a drop or two of dilute ammonia, and boiled down to about 15 c.c. The precipitate which forms is collected on a

<sup>1</sup> P. Dutoit and M. Duboux, *Bull. Soc. Chim.*, 1913 [iv], 13, 832.

small filter paper and washed with *boiling* water 6 times, using a very small quantity of water for each washing. The filtrate and washings are treated with a drop of ammonia, if they have become acid, and are boiled down to about 10 c.c., but as a rule no further precipitate will be obtained whilst the liquid is hot; any precipitate which forms on cooling can be neglected.

The filter papers with their precipitates are dried at 100° and burnt together in a platinum dish with a cover. The flame should be kept low until the whole is charred, and then gradually raised until the ash is white. The mass is then carefully treated with 30 c.c. of *N*-hydrochloric acid, and boiled until all is dissolved and all carbon dioxide expelled; the resulting solution is titrated with *N*/5 or *N*/2 sodium hydroxide, using phenolphthaleïn as indicator.

The sodium hydroxide is standardised by pure potassium hydrogen tartrate, and the *N*/1 hydrochloric acid by the alkali; phenolphthaleïn is used as indicator.

The number of c.c. of *N*/1 HCl used for the neutralisation of the ash  $\times$  0.070 gives the weight of citric acid in the portion tested.

An almost identical method has been described by L. and J. Gadais.<sup>1</sup>

If the citrate contains much sulphate it is advisable to ash at as low a temperature as possible, preferably with an alcohol flame. Before dissolving in hydrochloric acid, the ash should be treated with 10 c.c. of hydrogen peroxide. [If, as is usual, the hydrogen peroxide contains free acid, allowance must of course be made for it.]

**Lime Juice, Lemon Juice, and Factory Citric Acid Liquors.**—The analysis of these materials is conducted as follows: 15–20 c.c. of unconcentrated juice, or an amount corresponding with 3 c.c. of concentrated juice (40 grm. per 100 c.c.), previously diluted to facilitate exact measurement, are exactly neutralised with pure potassium hydroxide (*N*/5). The liquid, having a volume of about 50 c.c., is heated to boiling, mixed with a slight excess of concentrated calcium chloride solution, and kept at a gentle boil for half an hour. The precipitate is filtered off immediately while hot, washed with boiling water 6 times, and the mother liquor and washings again evaporated and worked up as described above under calcium citrate. The whole of the calcium citrate collected is then dissolved in 30 c.c. of *N*/1 hydrochloric acid and the excess of acid estimated as above. In dealing with the cruder factory liquors three or four evaporations are generally necessary to separate all the calcium citrate.

The above methods are not entirely free from error,<sup>2</sup> but have not yet been replaced by better. Incorrect results are obtained when the calcium citrate or juice contains other acids which yield sparingly soluble calcium salts. The presence of oxalic acid or of tartaric acid may be detected by the fact that the cold, neutralised solution gives a precipitate in the cold with calcium chloride.

<sup>1</sup> *Bull. Soc. Chim.*, 1909 [iv], 5, 287.

<sup>2</sup> Cf. O. von Spindler, *Chem. Zeit.*, 1903, 27, 1263.

**Other Methods of Estimation.**—The above-described methods are those which are generally adopted in the citric acid industry. The following

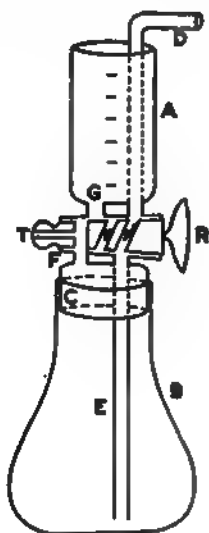


FIG. 5.

methods, selected from the numerous processes which have been suggested may be here briefly summarised.

C. Ulpiani and A. Parozzani<sup>1</sup> have described a method of analysis which, according to Klapproth (Lunge-Keane, Vol. III,) gives satisfactory results for citric acid even in presence of other organic acids. This method depends upon the fact that citric acid, in presence of a sufficient quantity of calcium chloride, is precipitated by sodium hydroxide *in the cold*, when the whole of the acid is saturated, and in the *hot* solution when one-third of the acid is saturated.

Spica<sup>2</sup> has described a method based on the formation of carbon monoxide when citric acid is gently warmed with concentrated sulphuric acid; 1 mol. of carbon monoxide is obtained for each mol. of citric acid present. The citric acid is first precipitated as calcium citrate (as in Warington's method) and the citrate then decomposed by the sulphuric acid in the apparatus described below (Fig. 5):

The upper part A, is fitted to the flask, B (150 c.c. capacity), by a ground joint, and the tubes, D and E and C and E, may be connected respectively through the tap, R, as also may the flask and the exterior. 2 grm. of the calcium citrate, moistened with water, are introduced into B, and the air in the flask is completely displaced by carbon dioxide, the absence of air being ascertained by means of an auxiliary nitrometer, filled with potassium hydroxide solution (1 : 5) and attached to the T-piece. 25 c.c. of concentrated sulphuric acid are then run into B from A, and a slow current of carbon dioxide is again passed into the flask, which is warmed to 80°–100° C., and occasionally shaken, the carbon monoxide evolved being collected in a nitrometer of 200 c.c. capacity, of which the lower part B<sup>1</sup> (100 c.c. capacity) is graduated in fifths of a cubic centimetre. When the volume of gas becomes constant, the nitrometer is allowed to stand for half an hour and then, after washing the gas with potassium hydroxide solution, introduced through I, the volume is read and the usual corrections are made for temperature and pressure. 1 c.c. of carbon monoxide at 0° C. and 760 mm. indicates 0.009407 grm. of citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O). The same apparatus may be used for the determination of carbonate in a citrate, by decomposing with a known volume of concentrated hydrochloric acid and measuring the evolved carbon dioxide over water.

The above process is obviously useless when other organic acids are present which evolve carbon monoxide.

**Estimation of Citric Acid in Presence of Other Acids.**—Beau's modification of the method of Denigès (*Ann. Chim. Phys.*, 1899, 18) is shown by Gowing-Scopes<sup>3</sup> to give unreliable results owing to the action of the hydrogen peroxide (added to remove the manganese dioxide) upon the precipitated mercury dicarboxysulphoacetone. Other reagents tried for removing the manganese dioxide either oxidised or reduced the precipitate, which in hot solutions was also oxidised by manganese dioxide. A compound containing

<sup>1</sup> *Atti. R. Accad. Lincei*, 1906 [v], 15, ii, 517.

<sup>2</sup> *Chem. Zeit.*, 1910, 34, 1141; compare Barboni, *Ann. Lab. Centr. delle Gabelle*, 1912, p. 311.

<sup>3</sup> *Analyst*, 1913, 38, 12.

72.5 to 74.0% of mercury and apparently similar to, if not identical with the compound of Denigès was obtained by the use of a reagent prepared by adding 68 c.c. of strong nitric acid to 51 grm. of mercuric nitrate and 51 grm. of manganese nitrate, diluting the mixture with 100 c.c. of water, and finally, making up the solution to 250 c.c. and filtering. For the determination of citric acid a quantity of the substance containing not more than 0.04 grm. nor less than 0.001 grm. of the acid is exactly neutralised with  $N/10$  alkali, using phenolphthaleïn as indicator, and, after the addition of 10 c.c. of the reagent, the liquid is diluted to 200 c.c., and boiled for 3 hours beneath a reflux condenser. The precipitate is washed by decantation, collected on a weighed Gooch crucible, and again washed in the crucible, which is then dried in the water-oven until nearly constant in weight (about 5 hours). The residue should then be of a cream colour, any yellow colouration indicating the formation of basic salts, which will cause the results to be too high. One-sixth of the weight of the precipitate gives the amount of citric acid. In 16 test estimations with pure citric acid within the limits stated above, the maximum error was  $+0.0003$  and  $-0.0004$  grm. Good results were also obtained in the presence of tartaric, succinic, oxalic, benzoic, and phosphoric acids, but when malic, lactic or salicylic acids were present the results were too high. Salicylic acid gives, with the reagent, a salmon-coloured precipitate, probably a nitro-derivative, whilst gallotannic acid gives an orange-brown precipitate. The precipitate given by citric acid decomposes suddenly when heated. It is very soluble in hydrochloric acid, in strong sulphuric or nitric acid, and in solutions of halogen salts.

In the absence of sugars it is not necessary to precipitate the citric acid as barium citrate and redissolve with phosphoric acid. The author claims an accuracy of 2% to 4%.

The above process does not give satisfactory results in presence of malic and tartaric acid and is therefore not applicable to the examination of fruit juices. In such cases, according to D. S. Pratt<sup>1</sup> the following method is of especial value.

50 grm. of fruit juice are treated with 110 c.c. of 95% alcohol to remove pectin bodies. After 15 minutes the solution is filtered and the residue washed with 95% alcohol. The resulting solution is diluted with water to an alcoholic strength of about 50%, and a 20% aqueous solution of barium acetate is added to precipitate the citric acid. After stirring, allowing the precipitate to settle, and filtering the solution, the precipitate on the paper is washed with 50% alcohol to remove sugars and then the paper and its contents are dried to remove the alcohol. The residue is then warmed with 50 c.c. of water and 3–5 c.c. of syrupy phosphoric acid to dissolve the barium citrate. This mixture is filtered into a graduated flask and the paper washed until the filtrate measures 100 c.c. An aliquot part of this solution containing 0.05–0.15 grm. citric acid is measured into a 500 c.c. dis-

<sup>1</sup> U. S. Dept. Agr. Bur. Chem., Circular 88 (1912).

tilling flask, 5–10 c.c. phosphoric acid are added with 400 c.c. hot water and the flask is heated. When briskly boiling 0.05% potassium permanganate solution is run in by means of a dropping funnel at the rate of 1 to 2 drops per second until the pink colouration is permanent.

The acetone formed by the oxidation distils off as fast as it is formed into 30–40 c.c. of Denigès<sup>1</sup> reagent. The distillation is continued till only 50–100 c.c. of solution remain in the flask.

The mixture in the receiver is then boiled gently under a reflux condenser for 45 minutes after the liquid becomes cloudy. It is then filtered hot through a Gooch crucible, washed with water, alcohol, and ether and dried in a water-oven for 30 minutes. The weight of precipitate multiplied by 0.22 gives the weight of citric acid originally present.

W. Fresenius and L. Grünhut<sup>2</sup> claim that the methods based on the precipitation of acetone dicarboxylic acid as given above are untrustworthy in the qualitative detection of citric acid in wines. For this purpose they recommend Krug's modification of Moslinger's test which is carried out as follows:

50 c.c. of wine are evaporated to a syrup. The syrup is treated with 95% alcohol and filtered to remove tartrates and then evaporated to remove alcohol. 10 c.c. of the resulting liquid are treated with acetic acid and lead acetate. In the presence of citric acid a precipitate will be obtained which dissolves on heating and reappears on cooling.

For recent data as to the composition of grape juices and notes on the determination of their acidity, see Gore.<sup>3</sup>

**Tests of Purity of Citric Acid, Lead, Arsenic, and Ash** are tested for as under tartaric acid, the limiting quantities allowed being the same as in the case of tartaric acid (see page 101). It is usual, however, in commerce to require a higher degree of freedom from lead than in the case of tartaric acid; the amount present seldom exceeds 10 parts per million. Arsenic is generally entirely absent.

**British Pharmacopœia 1914.**—The following are the requirements: 1 gm. dissolved in water requires for neutralisation 14.2 c.c. of *N*/1 solution of sodium hydroxide; yields no characteristic reaction for copper or iron and not more than very slight reaction for calcium or sulphates. *Lead limit* 20 parts per million. *Arsenic limit* 1.4 parts per million. 1 gm. of powdered citric acid mixed with 10 c.c. of sulphuric acid in a test-tube previously rinsed with sulphuric acid acquires not more than a pale yellow colour when kept at a temperature of 90° for 1 hour (absence of tartaric acid); ash not more than 0.05%.

The following colour tests, based on Pusch's method of detecting tartaric acid in citric acid are described by Hill.<sup>4</sup> 0.5 gm. of the sample and of pure

<sup>1</sup> Denigès reagent is made by adding 200 c.c. of concentrated sulphuric acid with constant stirring to a suspension of 50 gm. of mercuric oxide in 500 c.c. of water. This mixture is heated on a water-bath to ensure complete solution. It is then filtered, cooled and diluted to 1,000 c.c.

<sup>2</sup> *Zeit. anal. Chem.*, 1913, 52, 31.

<sup>3</sup> *J. Ind. Eng. Chem.*, 1909, 1, July.

<sup>4</sup> *Pharm. J.*, 1910, 84, 245.

citric acid are placed in separate test-tubes (6 in.  $\times$   $\frac{5}{8}$  in.) and 5 c.c. of sulphuric acid added to each. The tubes are placed simultaneously in an ordinary Bunsen flame; at the end of 30 seconds they are withdrawn and examined. The results obtained with acids of different degrees of purity are as follows:

Pure acid	= lemon-yellow solution.
5.0% of tartaric acid	= black, sulphur dioxide abundant.
1.0% tartaric acid	= deep brown-black, sulphur dioxide evident.
0.5% tartaric acid	= deep red-brown.
0.25% tartaric acid	= red-brown.
0.1% tartaric acid	= reddish-brown.
0.01% tartaric acid	= brownish-yellow.

With careful manipulation and 60 seconds heating, 0.0001% of tartaric acid is said to be easily detected; even 0.00001% gave a distinctly deeper tint, in good light, than the control tube. The test is also applicable to citrates, 1% of tartrate being easily detected. The above method is also applicable to detect sugar in citric acid; the reactions obtained are:

1% of sugar	= cherry-red, sulphur dioxide distinct.
0.1% of sugar	= sherry colour, sulphur dioxide evident.
0.01% of sugar	= yellowish-red, sulphur dioxide perceptible.
0.001% of sugar	= reddish-yellow.
0.0001% of sugar	= reddish-yellow.

It was also found that 0.5% of sugar could be detected, in tartaric acid, by the colouration after an hour's contact with cold sulphuric acid; by heating for 10 seconds in the flame the control tube remained practically unaffected, with 1% of sugar a red solution was obtained, and with 0.5% a red-brown ring.

Häussler<sup>1</sup> describes a characteristic colour reaction given by citric acid with vanillin; the solution is evaporated to dryness after adding an alcoholic solution of vanillin and the residue treated with 3 drops of dilute sulphuric acid, heated on a water-bath for 15 mins., dissolved in water and ammonia added. A bright-red colouration is obtained with 0.002 gm. of citric acid. The red colouration is not given by tartaric, malic, oxalic, malonic, benzoic, salicylic, acetic, lactic or succinic acids.

#### ERRATA IN VOL. I.

Page 537, line 4, for "solubltiy" read "solubility;" line 13 from bottom, for "mold" read "mould."

Page 543, line 8 from bottom, for "is" read "has been."

Page 545, line 11, "for "0.376" read 3.76."

<sup>1</sup> Chem. Zeit., 1914, 38, 937.



Page 546, line 4 for "flask" read "beaker;" line 8, for "10 c.c." read "100 c.c.;" line 10 from bottom, for "Warrington" read "Warrington."

Page 549 line 13, for "dissolved" read "treated."

Page 555, line 10, "Good lemons yield" should read "Good lemon juice yields."

Page 560, In the table at top of page, "Lime juice" "Lemon juice" should be interchanged.

Page 566, line 14 from bottom, "substracting" should read "subtracting;" line 13 from bottom, "form" should read "former;" line 8 from bottom, "hydroade" should read "hydroxide."

Page 573, in Index, insert "Gallisin," 304, 379. Delete "Læonlose," and insert after "Lævulose," p. 373.

Page 574, insert "Maltase," p. 361.

# FIXED OILS, FATS AND WAXES.

By C. AINSWORTH MITCHELL.

## EXTRACTION OF FAT.

Grimme<sup>1</sup> has made comparative estimations in which fat was extracted with various chlorohydrocarbons and with ether. The following average percentage results were obtained:

Ether	CHCl <sub>3</sub>	CCl <sub>4</sub>	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	C <sub>2</sub> HCl <sub>3</sub>	C <sub>2</sub> Cl <sub>4</sub>	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	C <sub>2</sub> HCl <sub>4</sub>
7.45	8.58	7.43	8.13	7.46	7.79	7.71	9.62

Only in the case of carbon tetrachloride and trichlorethylene did the results agree with those obtained with ether.

Complete extraction of the fat from cottonseed was not obtained with less than 100 c.c. of either cold solvent, but 45 minutes' extraction was sufficient with carbon tetrachloride and 30 minutes' with trichlorethylene.

With proportions below 10% of fat the weight of the residue left on evaporating 50 c.c. of the extract may be accepted as sufficiently accurate, but an addition of 0.2% should be made for amounts between 10 and 15%, and of 0.4% for amounts between 15 and 20%. Preliminary drying of the material was found by Grimme to be unnecessary.

Gowing-Scopes<sup>2</sup> confirms the suitability of cold trichlorethylene for the extraction of fat, but points out that it is advisable to dry the solvent to prevent the formation of the hydrochloric acid, which would act upon the fat.

He recommends for the extraction a modification of the apparatus devised by Beadle and Stevens<sup>3</sup>

The physical properties of the solvents are shown in the following table of Gowing-Scopes.<sup>4</sup>

Chlorohydrocarbon	Boiling point, °C.	Freezing point, °C.	Sp. gr. at 25°C.	Coefficient of expansion	Heat of vaporization, calories	Refractive index	Viscosity at 25°C.	Specific heat
Chloroform.....	61.5	.....	1.4791	0.001257	.....	1.449 (15°C.)	.....	.....
Carbon tetrachloride..	76.7	.....	1.5835	0.001227	.....	1.464 (15°C.)	.....	.....
Dichlorethylene, Cis....	48.8 (at 763 mm.)	.....	1.3328	0.001360	6930	.....	0.457	.....
Dichlorethylene, trans.	59.8 (at 763 mm.)	.....	1.3545	0.001270	7268	.....	0.510	.....
Trichlorethylene.....	87.5	- 73	1.4542	0.001193	7436	1.47914 (17°C.)	0.615	0.223
Tetrachlorethylene....	121.0	- 19	1.6080	0.001078	8554	.....	0.940	0.216
Tetrachlorethane.....	147.2	- 36	1.5881	0.000998	9134	1.49559 (17°C.)	1.808	0.268
Pentachlorethane.....	159.1	- 22	1.6712	0.000909	8829	.....	2.432	0.266
Hexachlorethane.....	185.5 (at 776.7 mm.)	- 187	2.01(?)	.....	.....	.....	.....	.....

<sup>1</sup> Chem. Rev. Fett. Ind., 1912, 19, 191.

<sup>2</sup> Analyst, 1914, 39, 4.

<sup>3</sup> Analyst, 1913, 38, 143.

<sup>4</sup> Analyst, 1914, 39, 5.

### Constitution and Chemical Properties.

**Theory of Saponification.**—Experiments in which triolein was fractionally saponified with alcoholic alkali have led Fortini<sup>1</sup> to the conclusion that saponification takes place in three distinct phases. The acetyl values of the fractions also supported the views of Lewkowitsch.

### Unsaponifiable Matter.

**Detection of Phytosterol and Cholesterol.**—Marcusson and Schilling<sup>2</sup> devised a method of separating phytosterol or cholesterol by precipitation with digitonin. A simple modification of the method is recommended by Fritzsche. 50 grm. of the melted fat are mechanically stirred for 5 minutes at 60° to 70° C. with 20 c.c. of a 1% alcoholic solution of digitonin. In the case of fluid and semi-solid fats the mass is at once filtered, with the aid of suction, in a Buchner's funnel, and the residue washed 6 times with ether (5 c.c. each time); in the case of solid fats 20 c.c. of chloroform are added to the hot liquid and the residue washed with two portions (4 c.c.) of hot chloroform and then with six portions of ether to remove all fat. The residue (digitonide) is dried for about 5 minutes at 30° to 40° C., dissolved in 2 c.c. of hot acetic acid, and the solution boiled for about 5 minutes in a test-tube with a vertical tube to act as condenser and then filtered through cotton wool. The tube and filter are twice washed with 0.5 c.c. of hot absolute alcohol, and the combined filtrate and washings evaporated on the water-bath in a current of air. The residual phytosteryl or cholesteryl acetate is dissolved in 0.5 to 1 c.c. of absolute alcohol and the crystals drained on porous porcelain and examined in the usual way (see also section on *Butter*).

**Alcoholysis.**—The method has been applied to the examination of castor and linseed oils by Haller<sup>3</sup> and of japan wax by Tassily.<sup>4</sup>

Elsdon<sup>5</sup> has submitted the process to critical examination and shows that although it determines the nature of the fatty acids contained in a fat, it is too tedious for ordinary laboratory work, and is only roughly quantitative. The results obtained may show the relative amounts of the constituents, but are probably not within 5 to 10% of the true values.

### Bromine and Iodine Absorptions.

**Insoluble Bromide Test.**—(See also under *Linseed Oil*, page 189.) Sutcliffe<sup>6</sup> recommends the following modification as giving results agreeing to within about 1%: 1 grm. of the oil is dissolved in 40 c.c. of ether in a weighed flask, 5 c.c. of glacial acetic acid are added, and the flask and its

<sup>1</sup> *Chem. Zeit.*, 1912, 36, 1117.

<sup>2</sup> *Chem. Zeit.*, 1913, 37, 1901.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1907, 26, 328; 1908, 27, 234.

<sup>4</sup> *Ibid.*, 1911, 30, 907.

<sup>5</sup> *Analyst*, 1913, 38, 8.

<sup>6</sup> *Analyst*, 1914, 39, 28, 338.

contents cooled in water to about  $11^{\circ}$ . Bromine is then added drop by drop until the solution is red, and the flask is closed and allowed to stand for 12 hours in water. The contents are filtered through a disc of paper in a Gooch crucible and the precipitate washed 3 times by decantation and twice in the crucible with 10 c.c. of ether chilled to  $5^{\circ}$ ; it is dried for 3 hours in the water oven, and weighed. Its melting point should range from  $141^{\circ}$  to  $144^{\circ}$  in the case of linseed oil.

Comparative determinations of the amounts of insoluble bromide and of the iodine value of linseed oils of various origin, showed that under these conditions the relationship between the two values could be expressed by the formula: Per cent. of bromide = (0.63 iodine value) — 78.0. The precipitated bromides must be white and crumble readily when dried. Certain sorts of bromine give products which when dried are dark and horny; these should be rejected.

Gemmell<sup>1</sup> was unable to obtain concordant results with various methods, mainly owing to the solubility of the bromides in the various solvents and he therefore recommends the following method, applied to the fatty acids, as being preferable to estimating the bromide obtained directly from the oils: The oil (5 grm.) is saponified with alcoholic potassium hydroxide, the soap dried and dissolved in 100 c.c. water, and the fatty acids liberated in the usual way. The flask is cooled in water, and the fatty acids separated by shaking with ether. The united ether extract (100 c.c.) is divided into aliquot portions (20 c.c.), and to each of these is added 2 c.c. of glacial acetic acid. The flasks are chilled in ice-water and the solution brominated and allowed to stand, the liquid decanted, the precipitates washed thrice in the flasks with chilled ether, then transferred (by means of 5 c.c. of ether) to a weighed filter paper, dried and weighed.

The following results were thus obtained: Raw linseed oils (7 kinds) 32.60 to 37.65; boiled linseed oils (6 samples), 25.95 to 33.90; soja bean oil, 4.10; rape oil, 2.35; and walnut oil, 3.0%; china wood oil, *nil*. Satisfactory results may also be obtained in the way with marine animal oils, as is shown by the following typical examples: Cod-liver oil, 35.20; whale oil, 21.70; brown whale oil, 25.80; menhaden oil, 51.70; shark-liver oil, 17.70; and sperm oil, 1.70.

The main objection to Gemmell's modification is the risk of loss of linolenic acid by oxidation during the liberation of the fatty acids. Some of his criticisms upon the direct methods have been answered by Sutcliffe.<sup>2</sup>

The loss due to solubility might possibly be overcome, at all events in the case of linseed oil, by previously saturating the solvent with the insoluble bromide purified by extraction with ether.

Gemmell (*loc. cit.*) points out that the solubility of the bromide from marine animal oils is less than that of the bromide from vegetable oils, so

<sup>1</sup> *Analyst*, 1914, 39, 297.

<sup>2</sup> *Analyst*, 1914, 39, 388.

much so that a precipitate is formed as soon as bromine is added. He suggests that this affords a rapid means of detecting fish oils in vegetable oils.

In his opinion the insoluble bromide formed by linseed oil is not that of a mixed glyceride, but the reasons given in support of this view are not conclusive.

Stiepel has found<sup>1</sup> that the amount of insoluble bromide from linseed oil is greatly reduced by heating the oil, while the analogous bromide obtained from marine animal oil is no longer formed after heating. Hence a negative result of the "octobromide" test cannot of itself be regarded as a proof of the absence of marine animal oil.

Thus the commercial product *neutraline*, which consists of deodorised fish oil, yields no insoluble bromide, and might therefore be taken for an animal hoof oil.

**Iodine Value.**—Comparative determinations of the iodine values of erucic, elaidic, oleic, ricinoleic and undecylic acids, made by Weiser and Donath<sup>2</sup> by the methods of Hübl, Waller, Wijs and Winkler, gave practically concordant results. In the case of linoleic acid the only method that gave theoretical results was that of Winkler, the other methods giving too high values. The iodine values of crotonic, tiglic and cinnamic acids could not be determined by the methods of Hübl, Waller and Wijs, whereas nearly theoretical results were obtained by Winkler's method.

**Winkler's Method.**<sup>3</sup>—From 0.1 to 0.5 gm. of the fat is dissolved in 10 c.c. of carbon tetrachloride, and the solution treated with 50 c.c. of Winkler's solution (*N*/10 potassium bromate solution containing 1 to 1.5 gm. of potassium bromide and 10 c.c. of 10% hydrochloric acid). After 30 minutes to 2 hours (according to the degree of unsaturation of the fat) 10 c.c. of 10% potassium iodide solution are added and the liberated iodine titrated with thiosulphate solution.

Meigen and Winogradoff<sup>4</sup> show that unsaturated fatty acids (oleic acid) absorb more chlorine than iodine from a mixture of the 2 halogens, while more or less substitution of the chlorine occurs. This substitution is checked by the presence of acid. It is inadvisable, however, to add a large excess of hydrochloric acid (as in Waller's solution) since combination of oleic acid with the hydrochloric acid will then take place. In examining an unknown compound Meigen and Winogradoff advocate the use of Wijs' method, with the addition that after the titration with thiosulphate the product of the action is extracted with water, and the amount of halogen acid in the aqueous extract is titrated with *N*/10 alkali.

Thus a sample of pure oleic acid treated for 30 minutes with a Wijs' solution containing 13 gm. of iodine per 1,000 c.c. and an equivalent quantity of chlorine gave an iodine value of 99.95 (theory, 89.95), while the acid

<sup>1</sup> *Chem. Zent.*, 1912, 2, 175.

<sup>2</sup> *Zeit. Untersuch. Nahr. Genussm.*, 1914, 28, 65.

<sup>3</sup> *Pharmacop. Hungarica*, 1900, XI.

<sup>4</sup> *Zeit. angew. Chem.*, 1913, 27, 241.

in the aqueous solution corresponded to 4.62% of substituted iodine. With a Wijs' solution containing an excess of 2% of iodine over the chlorine the iodine value found was 90.95, while the acid in the aqueous extract corresponded to 0.53% of substituted iodine. When there was an excess of 10% of chlorine in the Wijs' solution the iodine value of the oleic acid was 105.40, and the acid in the aqueous solution corresponded to 8.31% of iodine. It was proved that halogen acids were only formed by substitution.

Gowing-Scopes<sup>1</sup> studied the effect of using different chlorohydrocarbons as solvent in Wijs' method and found that the results obtained with trichlorethylene, tetrachlorethylene, tetrachlorethane and pentachlorethane agreed closely with those obtained with carbon tetrachloride, but that the figures with dichlorethylene were too low.

**Acetyl Value.**—To obtain results comparable with the other values of fat analysis Holland<sup>2</sup> suggests that the acetyl value should indicate the number of milligrams of potassium hydroxide required to saponify the acetyl taken up by 1 grm. of the fat on acetylation.

It may be rapidly determined as follows: 5 grm. of the fat are heated with 10 c.c. of acetic anhydride over boiling water beneath a reflux condenser for 1½ hours, sufficient ceresin to form a solid disc when cold being then introduced. After the addition of 150 c.c. of boiling water the flask is again heated on the water-bath, occasionally shaking, to expel acetic acid and then cooled. The solid cake is again heated with 150 c.c. of boiling water, and this process repeated about 6 times, until the filtrate is nearly neutral.

The solid disc and particles on the filter are now boiled with 50 c.c. of standard alcoholic potassium hydroxide solution and 50 c.c. of alcohol, beneath a reflux condenser (with glass beads to prevent bumping) and the excess of alkali titrated with standard hydrochloric acid.

The difference between the saponification values before and after acetylation is the acetyl value.

### Oxidation of Oils—Drying Properties.

**Gravimetric Estimation of Absorption of Oxygen during Drying.**—A method devised by Krumbhaar<sup>3</sup> of measuring the amount of oxygen absorbed by oils during drying may also afford a means of distinguishing between different drying oils. A weighed quantity of the oil is mixed with 0.6% of cobalt resinate and spread over filter paper, which is placed in a U-tube immersed in water at 30° C. A steady current of dry air (free from carbon dioxide) is drawn through this tube, and the volatile products formed in the drying process are passed, first through a strongly heated tube of copper oxide (to complete their decomposition into carbon dioxide and water) and

<sup>1</sup> *Analyst*, 1914, 39, 19.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1914, 6, 482.

<sup>3</sup> *Chem. Rev. Fell. Ind.*, 1913, 20, 290.

then through weighed absorption tubes containing calcium chloride and soda-lime. After every 2 hours the air in the apparatus is replaced by nitrogen, the taps closed, and the tube containing the oil and the absorption tubes weighed, this being continued until the weight becomes constant. The sum of the increase of weight in the oil tube, of the hydrogen absorbed by the calcium chloride tube and of the carbon absorbed by the soda-lime tube gives the amount of oxygen taken up by the oil.

For example, 0.743 grm. of linseed oil showed an increase in weight of 0.128 grm. in 18 hours, while the amounts of hydrogen and carbon volatilised were 0.009 and 0.016 grm. respectively, giving a total of 0.153 grm. or 20.6% of oxygen absorbed by the oil. (See also under Linseed Oil, page 193.)

### Colour Tests of Oils.

Colour indications given by oils with certain phenols in the presence of nitric acid are described by Malacarne.<sup>1</sup> The most distinctive is the violet colouration given by sesame oil with resorcinol or phloroglucinol.

### Catalytic Hydrogenation of Oils—Hardened Oils.

During the last 3 years the analytical problems in the examination of fats have been greatly complicated by the general introduction of hydrogenated oils as commercial products.

Theoretically it should be possible to convert oleic, linoleic and other unsaturated fatty acids and glycerides into the corresponding solid acids of the stearic series by the simple addition of hydrogen, the process being analogous to the absorption of halogens or oxygen by the unsaturated compounds



Prior to 1902, however, all attempts to hydrogenate oils by this method proved unsuccessful, but in that year Le Prince and Siveke (Germ. Pat. 141029) claimed a process of solidifying oils by heating them with hydrogen in the presence of a catalytic agent; and an analogous English patent (No. 1515 of 1905) was taken out by Normann.

The development of the new industry and the types of apparatus used in the various processes are described by Ellis.<sup>2</sup> See also Crossley.<sup>3</sup>

The catalytic agents most commonly used in the commercial processes are nickel and its salts, and palladium salts, which are usually precipitated in a fine state of division over a porous material such as pumice stone, or kieselguhr. Other catalysts include cobalt, iron, platinum, and osmium, and their oxides and other salts. The presence of traces of the catalytic

<sup>1</sup> *Chem. Zentr.*, 1913, 1, 2183.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1912, 31, 1155.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1914, 33, 1135.



agent, especially nickel, in the hardened fats sometimes affords a proof of the origin of the material.

**Commercial Hardened Oils.**—Speaking generally the solidified products obtained by hydrogenating whale and fish oils are only used for technical purposes such as soap-making. Examples of such fats are *talgol* and *candelite*, which are made at Emmerich.

Edible hardened oils, prepared from cottonseed, sesame and other oils are being increasingly used in Europe and America in the preparation of margarine and lard substitutes. One of the best known German edible hardened oils is sold under the name of *brebesol*. The physical condition of the products ranges from a semi-solid mass resembling butter to a hard tallow, according to the degree of hydrogenation of the oil.

**Analytical Constants of Hardened Oils.**—(See also under Margarine page 173). Hydrogenation of an oil lowers its refractometer reading and iodine value, and raises its melting point, but has little effect upon the saponification value.

The following results were obtained by Bömer and Leschly-Hansen<sup>1</sup> in the examination of oils hardened by heating in an autoclave in a current of hydrogen in the presence of nickel reduced on kieselguhr.

Oil	M. p. °C.	Solid. pt. °C.	Refractometer reading at 40° C.	Acid value	Sapon. value	Iodine value
Arachis.....	51.2	36.5	50.1	1.0	188.7	47.4
Sesame.....	47.8	33.4	51.5	0.5	190.6	54.8
Sesame, technical.....	62.1	45.3	{ 38.4 } (at 50° C.)	4.7	188.9	25.4
Cottonseed.....	38.5	25.4	53.8	0.6	195.7	69.7
Whale.....	45.1	33.9	49.1	1.2	192.3	45.2
Coconut, natural.....	25.6	20.4	37.4	0.3	255.6	11.8
Coconut, hardened.....	44.5	27.7	35.9	0.4	254.1	1.0

The liquid fatty acids showed the following iodine values: Hardened arachis oil, 82.9 to 91.8; sesame oil, 88.9; cottonseed oil, 115.6; and whale oil 96.0.

The reduction in the refractive index caused by hydrogenation is shown by the following examples given by Ellis:<sup>2</sup> Maize oil, 1.4514; whale, 1.4550; soja bean, 1.4538; coconut "olein," 1.4425; linseed 1.4610; palm, 1.4517; and arachis oil, 1.4547.

*Hardened marine animal oils* are deodorised in the process, and acquire the appearance of tallow. Two samples analysed by Grimme<sup>3</sup> gave the following values:

Sp. gr. at 15° C.	M. p °C.	Solid. pt. °C.	Refractive index at 40° C.	Acid value	Sapon. value	Iodine value (Wijs)
0.9271	47.2	34.9	1.4529	1.94	189.3	23.24
0.9256	38.5	31.5	1.4575	1.00	188.8	58.34

<sup>1</sup>Chem. Rev. Fett. Ind., 1912, 19, 218, 247.

<sup>2</sup>J. Ind. Eng. Chem., 1914, 6, 117.

<sup>3</sup>Chem. Rev. Fett. Ind., 1913, 20, 129.

**Colour Tests.**—Hardened marine animal oils often give intense colourations with concentrated mineral acids, but these do not agree with colourations described as characteristic of the untreated oils. The intensity of the colouration varies with the degree of hydrogenation. Sulphuric acid containing a trace of iodine gives a violet-red colouration with hardened whale and fish oils.

Bellier's reagent for seed oils (nitric acid, sp. gr. 1.4 and resorcinol in benzene) gives somewhat different shades of colour with hardened sesame, arachis and cottonseed oils than in the case of the original oils. With hardened marine animal oils both acid and oil give an orange-yellow colouration.<sup>1</sup>

Arachidic acid may be detected in hardened arachis oil (*q.v.*) but a suitable modification is required.

The Baudouin test for sesame oil is intensified, whereas Haphen's cottonseed oil test is inhibited. Hauchehorne's test for cottonseed oil (*q.v.*) is not affected.

According to Leimdörfer<sup>2</sup> the stearic acid formed in the hydrogenation of oils is chemically identical with natural stearic acid, but the stearin of hydrogenated oils differs in crystalline character and other physical properties from the stearin of ordinary fats.

Hydroxyl groups are more or less split off in the hydrogenating process. Thus the hydroxyl value of a sample of castor oil fell from 156 to 102.<sup>3</sup>

The proportion of insoluble bromides given by linseed and marine animal oils is greatly reduced by hydrogenation, so that the insoluble bromide test will not give the same result as before and may even fail to detect the presence of these oils.

**Unsaponifiable Matter.**—Hydrogenation also reduces the amount of cholesterol or phytosterol in the oil, and in proportion to the degree of hardening. The process affects cholesterol more than phytosterol. Thus it has been found by Marcusson and Meyerheim<sup>4</sup> that 75% of cholesterol was resinified during hydrogenation at 200°, whilst phytosterol was not appreciably affected. After treatment at 250° cholesterol no longer gave any crystalline derivatives.

This explains why cholesterol cannot be isolated from *talgol* and similar hardened products of animal oils.

**Detection of Nickel in Hardened Oils.**—Bömer and Leschly-Hansen (*loc. cit.*) recommend the dimethylglyoxime test: From 5 to 10 gm. of the fat are mixed with strong hydrochloric acid in a test-tube which is immersed with frequent shaking for 30 minutes in boiling water. The acid extract (filtered if necessary through animal charcoal) is then evaporated and the residue tested with a 1% alcoholic solution of dimethylglyoxime.

Bömer<sup>5</sup> found 0.01% of ash with 0.006% of nickel oxide in hydrogenated

<sup>1</sup> Kreis and Roth: *Z. Untersuch. Nahr. Genussm.*, 1913, 25, 81.

<sup>2</sup> *Chem. Zentralbl.*, 1914, 1, 304.

<sup>3</sup> Normann and Hugel: *Chem. Zeit.*, 1913, 37, 815.

<sup>4</sup> *Zeit. angew. Chem.*, 1914, 27, 201.

<sup>5</sup> *Chem. Rev. Fett Ind.*, 1912, 19, 221.

sesame oil and 0.006% of ash with 0.0045% of nickel oxide in hardened whale oil.

The physiological significance of traces of nickel in hardened oils is discussed by Ellis,<sup>1</sup> Knapp,<sup>2</sup> Bömer (*loc. cit.*); and Offerdahl-Larvik.<sup>3</sup>

It has been found by Prall that in some cases pure untreated oils may give a red colouration; while Kerr<sup>4</sup> has shown that hydrogenated cottonseed oil free from nickel may yield to hot hydrochloric acid an organic base, which will give with dimethylglyoxime and ammonia a red colouration, closely resembling that obtained with traces of nickel except that it is fugitive. Hence before applying the test for nickel the residue should be treated with 2 to 3 c.c. of nitric acid to destroy organic matter. Owing to this uncertainty, Knapp<sup>5</sup> prefers the less sensitive ammonium sulphide test: 50 grm. of the fat are heated with 20 c.c. of hydrochloric acid with vigorous shaking, the acid extract is evaporated to dryness, and the residue dissolved in 1 drop of water, and tested on a white tile with 1 drop of ammonium sulphide (compare also page 173).

<sup>1</sup> *J. Soc. Chem. Ind.*, 1912, 31, 1166.

<sup>2</sup> *Analyst*, 1913, 38, 102.

<sup>3</sup> *Ber. deutsch. Pharm. Ges.*, 1913, 23, 558.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1914, 6, 207.

<sup>5</sup> *Analyst*, 1913, 38, 102.

# SPECIAL CHARACTERS AND MODES OF EXAMINING FATS, OILS AND WAXES.

By E. R. BOLTON AND CECIL REVIS.

## ARACHIS OIL.<sup>1</sup>

The Indian or Mozambique nuts are usually decorticated before shipment to Europe. As they undergo "heating" on the voyage they cannot be used to produce the best edible oil and are mainly worked up for soap oils. The Bombay nuts yield a somewhat better quality and the largest nuts are those cultivated in Fiji. The greatest quantity of Arachis nuts comes from Senegal.

Bellier's test has been very carefully investigated by Evers<sup>2</sup> who has confirmed the statement made in Vol. II, that low results are obtained by this process as usually carried out.

He has compared the method with Renard's process and obtained the following results:

TABLE I.

Oil	Renard			Bellier		
	Arachidic acid, %	M. p., °C.	Arachis oil, %	Arachidic acid, %	M. p., °C.	Arachis oil, %
Arachis (A).....	4.59	73.5	.....	3.56	71	78
Arachis (B).....	5.15	72.0	.....	3.76	71	83
Olive oil, Nice superfine.....	0	.....	.....	0	.....	.....
Olive oil, "seconds".....	0	.....	.....	Trace	.....	.....
Olive oil, Malaga.....	0	.....	.....	Trace	.....	.....
Olive oil, 50 % } Arachis (A), 50 % }	2.28	73.5	50	1.36	72	30

Evers suggests that the low results obtained may be due either to the solubility of arachidic and lignoceric acids in 70% alcohol or to the incomplete precipitation of the fatty acids on account of their solubility in the strong solution of oleic and other fatty acids. Renard<sup>3</sup> states that arachidic and lignoceric acids are quite insoluble in 70% alcohol, but Evers contests this statement and having prepared these acids from arachis oil by Renard's process, obtained the following mean values for their solubility in 70% alcohol under the stated conditions.

<sup>1</sup> Lewkowitsch, *Chem. Tech. Oils and Fats*, Ed. v, 2, 298.

<sup>2</sup> *Analyst*, 1912, 37, 487.

<sup>3</sup> *Compt. rend.*, 73, 1330.

About 0.2 gm. fatty acid was dissolved in 93% alcohol and sufficient water added to reduce the strength of alcohol to 70%. After standing for several hours the liquid was filtered and a measured volume evaporated to dryness, the solubilities given below being calculated from the weight of residue.

TABLE II.

Melting point	Solubility, grams per 100 c.c.	
	At 13° C.	At 18° C.
71° C.	0.015	0.023
72° C.	0.012	0.017
73° C.	0.009	0.012

The solubility was also determined when the fatty acids were washed on a filter paper, about 0.2 gm. being used.

Thus:

M. p., °C.	Grams dissolved per 100 c.c.
71	0.008
72	0.006
73	0.005

From the foregoing and other figures, the author has drawn up Table III giving the corrections for practical working and as a result of his experiments he has modified the process as given below.

TABLE III.

Weight of acids (corrected for 90 % alcohol)	Correction per 100 c.c., 70 % alcohol		
	M. p., 71°	M. p., 72°	M. p., 73°
Above 0.10 gm.....	0.013 gm.	0.008 gm.	0.006 gm.
0.08-0.10 gm.....	0.011 gm.	0.007 gm.	0.005 gm.
0.05-0.08 gm.....	0.009 gm.	0.007 gm.	0.005 gm.
0.02-0.05 gm.....	0.007 gm.	0.006 gm.	0.005 gm.
Less than 0.02 gm.....	0.006 gm.	0.005 gm.	0.004 gm.
Factor for conversion of percentage of fatty acids to arachis oil.	17	20	22

**Modified Renard's Process.**—Weigh out 5 gm. of the oil into a flask, add 25 c.c. of alcoholic potassium hydroxide (80 gm. potassium hydroxide dissolved in 80 c.c. water and diluted to a litre with 90% (by vol.) alcohol), and saponify for about 5 minutes under a reflux condenser. To the hot soap solution add 7.5 c.c. of acetic acid (1 vol. of glacial acetic acid to 2 vol. of water) and 100 c.c. of 70% alcohol containing 1% (by vol.) of HCl, and cool to 12° to 14° for an hour. Filter and wash with 70% alcohol containing 1% of HCl at 17° to 19°, the precipitate being broken up occasionally by means of a platinum wire bent into a loop. The washing is continued until the filtrates give no turbidity with water, the washings being measured. Dissolve the precipitate, according to its bulk, in 25 to 70 c.c. of hot 90% alcohol, and cool to a fixed temperature between 15° and 20°. If crystals appear in any quantity, allow to stand at this temperature for 1 to 3 hours, filter, wash

with a measured volume of 90% alcohol (about half the volume used for crystallisation), and finally with 50 c.c. of 70% alcohol. Wash the crystals with warm ether into a weighed flask, distil off the ether, dry at 100°, and weigh. If the melting point is lower than 71°, recrystallise from 90% alcohol. Add the correction for the solubility in 90% alcohol as in Renard's process, from the table given by Archbutt (see Vol. II, p. 94), and also for the total volume of 70% alcohol used in the precipitation and washing (including the 100 c.c. added in the first instance) from Table III.

If there are no crystals from 90% alcohol, or only a very small amount, add a sufficient quantity of water to reduce the strength of the alcohol to 70% (31 c.c. of water to 100 c.c. of 90% alcohol). Crystallise at 17° to 19° for an hour, filter, wash with 70% alcohol and weigh as before, adding the correction for 70% alcohol from Table III. If the melting point is below 71° recrystallise from a small quantity of 90% alcohol, or again from 70% alcohol.

TABLE IV.

Oil	Alcohol used for crystallisation, %	Weight of crystals	Correction for 90 % alcohol	Correction for 70 % alcohol	Total	%	M.p., ° C.	% of arachis oil by factor
		Grm.	Grm.	Grm.	Grm.			
Arachis (A)..... {	90	0.160	0.040	0.027	0.227	4.54	73	100
	70	0.218	.....	0.065	0.283	5.66	71	96
Arachis (B)..... {	90	0.163	0.045	0.032	0.240	4.80	72	96
	70	0.233	.....	0.068	0.301	6.02	71	102
Arachis (C).....	90	0.152	0.054	0.034	0.240	4.80	72	96
Arachis (D).....	90	0.194	0.033	0.028	0.255	5.10	72	102
Arachis (A), 50 %....	90	0.056	0.032	0.022	0.110	2.20	73	48
Olive "Nice," 50 %....	70	0.090	.....	0.055	0.145	2.90	71	49
Arachis (A), 35 %.. } Olive "Nice," 65 %.	90	0.045	0.020	0.029	0.094	1.88	71	32
	90	0.029	0.040	0.020	0.089	1.78	72.5	37
	70	0.059	.....	0.040	0.099	1.98	71	34
Arachis (A), 20 %....	90	0.024	0.012	0.019	0.055	1.10	71	19
Olive "Nice," 80 %...	70	0.030	.....	0.024	0.054	1.08	71	18
Arachis (C), 20 %....	90	0.012	0.020	0.015	0.047	0.94	72	19
Olive "Malaga," 80 %	70	0.021	.....	0.027	0.048	0.96	71	16
Arachis (A), 10 %....	90	0.009 <sup>2</sup>	0.008	0.008	0.025	0.50	73	11
Olive "Nice," 90 %...	70	0.008	.....	0.015 <sup>1</sup>	0.023	0.46	70	8
Arachis (B), 10 %....	90	0	.....	.....	.....	0	.....	.....
Olive "Nice," 90 %...	70	0.012	.....	0.018	0.030	0.60	71	10
Arachis (C), 10 %....	90	0	.....	.....	.....	0	.....	.....
Olive "Malaga," 90 %	70	0.011	.....	0.016	0.027	0.54	71	9
Arachis (A), 5 %.... } Olive "Nice," 95 % }	70	0.007	.....	0.012 <sup>1</sup>	0.019	0.38	.....	6.5
Sesame..... {	90	0	.....	.....	.....	0	.....	.....
	70	0.012	.....	.....	.....	0.24	64	.....
Cottonseed..... {	90	0	.....	.....	.....	0	.....	.....
	70	0.006	.....	.....	.....	0.12	50-55	.....
Olive "saponified". {	90	0.014	.....	.....	.....	0.28	64-67	.....
	70	0.021	.....	.....	.....	0.42	64-68	.....

<sup>1</sup> In these cases the correction has been added for melting point 71°.  
<sup>2</sup> This result was obtained by recrystallising the fatty acids obtained from 70 % alcohol from 10 c.c. of 90 % alcohol.

The results obtained by this method are given in Table IV.

The following oils gave no crystals: Olive oils, including "Nice superfine," "Nice seconds," "Malaga," and eight of unknown origin, almond, poppy and rape oils. "Saponified" olive oil on the other hand usually gives crystals (see olive oil, page 132).

The qualitative method of Bellier has been shown by Franz and Adler<sup>1</sup> to be capable of yielding approximately quantitative results by determining the temperature at which turbidity is first produced. For this purpose they give the following table of "temperatures of crystallisation."

Oil	Temperature of crystallisation	Oil	Temperature of crystallisation
	°C.		°C.
Olive oil.....	11.8-14.3	Arachis oil, 50%.....	33.8
Arachis oil, 5%.....	15.9-17.0	Arachis oil, 60%.....	35.3
Arachis oil, 10%.....	19.8	Arachis oil, 70%.....	36.6
Arachis oil, 20%.....	25.7	Arachis oil, 80%.....	38.0
Arachis oil, 30%.....	29.2	Arachis oil, 90%.....	39.3
Arachis oil, 40%.....	31.5	Arachis oils.....	40.0-40.8

The present revisers have had the opportunity of noting these "temperatures of crystallisation" for a considerable number of mixtures and find them to give most useful indications, which are approximately correct in the majority of cases. In connection with this application of the test, H. Lüers<sup>2</sup> draws attention to a turbidity given by certain olive oils which were proved to be free from arachis oil, and he states that the addition of 3 drops of glacial acetic acid, in addition to the dilute acetic acid, prevents the formation of this turbidity.

### ALMOND AND APRICOT-KERNEL OILS.

Ross and Race<sup>3</sup> have compared certain analytical figures for these two oils, and for the fatty acids obtained from them by fractional distillation; from their results they deduce that the composition of the two oils is so similar that they may, for practical purposes, be considered identical.

This statement is most unfortunate and misleading, for it is obvious that the purchaser of almond oil would be greatly defrauded if he were to be sold apricot-kernel oil, which is usually less than half the price. C. A. Hill (*ibid.*) records his disagreement with the statement that the oils may be considered as identical. The same authors have shown that notwithstanding the similarity in general composition, apricot-kernel oil is distinguished by means of the Bieber reaction (Vol. II, p. 104) and that the chromogenic substance, which is not volatile, is not destroyed by subjecting the oil to steam distillation for some hours. Moreover, they found that even in the case of a sample a year old, through which air was blown while warm for 3

<sup>1</sup> Abs. J. Soc. Chem. Ind., 1912, 30, 691.

<sup>2</sup> Zeit. Unters. Nahr. Genussm., 1912, 24, 683.

<sup>3</sup> Analyst, 1911, 36, 263.



days, the Bieber reaction was still so strong that as little as 5% could be detected when mixed with almond oil.

The following table gives the limits of the figures obtained from the analysis of 4 samples of almond and 3 samples of apricot-kernel oil bought commercially and for 1 sample sold as peach-kernel oil.

	Limits of four samples of almond oil	Limits of three samples of apricot-kernel oil	Peach kernel
Iodine value.....	97 to 102	100 to 106	101.6
Saponification value.....	183.3 to 207.6	184 to 192.4	191.7
Sp. gr., $\frac{15^{\circ}}{15^{\circ}}$ .....	0.9178 to 0.9199	0.9198 to 0.9200	0.9167
Ref. index at 40° (Zeiss).....	57.5° to 58°	57° to 58.5°	55.5°
Bieber reaction.....	nil.	strong	strong

FATTY ACIDS.

Saponification value.....	200.4 to 207	197 to 202	201.6
Ref. index at 40° (Zeiss).....	56° to 58°	57° to 59°	53°

The acidity of 23 samples of almond oil has been determined by J. C. Umney<sup>1</sup> who found it to range from 0.6 to 9.2% for acid calculated as oleic, and that an oil of high acidity was satisfactory in odour and lustre after keeping 6 months. Apricot oil, on the other hand, was not satisfactory in these respects after 12 months. 34 samples of peach and apricot-kernel oils were found to have acidities ranging from 0.6 to 5.97% (as oleic acid). Lewkowitsch<sup>2</sup> gives the following table of figures.

Description of oil	Sp. gr.	Saponi- fication value	Iodine value.	Butyro- refracto- meter at 40° C. Degrees.	Free fatty acids <sup>3</sup>	Fatty acids.		Bieber's test
						Neutral- isation value	Saponi- fication value	
Almond oils expressed from:								
1. Valencia sweets....	0.91995	207.6	99.4	57.5	2.61	207.8	207.6	Colourless
2. Blanched valencia sweets.	0.9182	191.7	103.6	57.5	1.46	196.4	201.7	Colourless.
3. Sicily sweets.....	0.9178	183.3	100.3	57.0	0.39	198.8	202.2	Colourless.
4. Masagan bitters....	0.9180	188.6	102.5	56.5	1.56	196.8	203.1	Colourless.
5. Small Indian almonds.	0.91907	189.2	96.65	57.0	1.46	195.8	200.7	Colourless.
6. Mogador bitters....	0.9183	194.98	104.2	57.0	0.65	197.1	203.2	Colourless.
7. Peach-kernel oil....	0.9198	191.4	95.24	57.5	1.51	196.8	205.0	Colourless at first, then pink.
8. Apricot-kernel oil...	0.9200	192.4	107.4	58.0	1.16	198.0	202.0	Pink colouration.
9. Apricot-kernel oil from Mogador kernels.	0.9172	198.2	107.9	57.0	1.41	194.0	200.7	Slightly pink.
10. Californian apricot-kernel oil.	0.92026	190.3	108.7	58.0	0.61	197.8	202.8	Very slightly pink.

<sup>1</sup> *Perf. and Essent. Oil Record*, 1914, 5, 101.  
<sup>2</sup> *Analyst*, 1904, 29, 106.  
<sup>3</sup> Calculated by present revisers from acid values.

## OLIVE OIL.

Rape oil in olive oil is best detected by Tortelli and Fortini's method.

In carrying out this test the following details must be adhered to *exactly*. 20 grm. of the oil are saponified with 6 grm. of potassium hydroxide dissolved in 50 c.c. of 90% alcohol by heating under a reflux condenser. The liquid is neutralised to phenolphthalein with 10% acetic acid and the solution then slowly poured into a boiling mixture of 200 c.c. of 10% lead acetate and 100 c.c. of water, shaking vigorously during the addition. The mixture is cooled under the tap, maintaining a rotary motion until the soaps begin to stick to the sides (if they do not stick at first, they will do so during the first washing). The water is poured off and the soaps washed 3 times with 200 c.c. of warm (60 to 70°) water, the water being then drained off and, as far as possible, removed with filter paper. To the dried soaps 80 c.c. of methylated ether are added and the whole is well shaken for several minutes till the mass is broken up, when it is heated under a reflux condenser for 30 minutes, shaking at intervals. The flask is then closed and placed in water *at exactly* 15° C. *for 1 hour*, after which the contents of the flask are poured on to a filter, the funnel being placed in the mouth of a separator and the filter closely covered till all the ether possible has filtered out. The filter and contents are dropped back into the flask and the ether treatment (boiling and cooling) is repeated in exactly the same way, using 40 c.c. of ether, and the mass filtered as before, again tightly covering the filter and allowing to drain as completely as possible. The flask is washed out with a further 40 c.c. of ether on to the filter, the contents of which are well stirred up with the ether, which is then allowed to drain off. The combined ethereal solutions of the lead salts so obtained are decomposed in the separator by shaking twice with 150 c.c. of 10% hydrochloric acid, after which the ether is washed with two quantities of 100 c.c. of water, the ethereal solution being then run out into a dry flask and allowed to evaporate spontaneously or by the use of gentle warmth in a current of hydrogen. The liquid fatty acids so obtained are dissolved in 40 c.c. of strong alcohol (97 %) and a saturated solution of sodium carbonate added until the liquid is saturated (sodium carbonate separates). The alcohol is distilled off and the residue dried, first in the water oven, distributing it as much as possible over the sides of the flask, and finally in a vacuum desiccator for at least 48 hours. The dry sodium soaps are then boiled with 50 c.c. of *absolute* alcohol and filtered in a hot funnel, the insoluble residue being boiled with a further quantity of alcohol and the treatment repeated till nearly the whole has been dissolved. The mixed alcoholic filtrates are freed from alcohol by distillation and the sodium soaps dried as completely as possible in a vacuum desiccator over sulphuric acid.

According to Tortelli and Fortini the test is concluded as follows:

0.5 grm. of the dry soaps are placed in a large test-tube and dissolved by

heating in 20 c.c. of absolute alcohol. A thermometer is then placed in the mixture, which is allowed to cool and the turbidity temperature noted.

The following table gives some results obtained by them:

Oil	Turbidity temperature, °C.
Olive.....	20-24°
Rape.....	45-50°
1 pt. olive } .....	35-40°
1 pt. rape } .....	
8 pt. olive } .....	30-35°
2 pt. rape } .....	
9 pt. olive } .....	30-34°
1 pt. rape } .....	
Cotton.....	14-16°
Sesame.....	18-20°
Arachis.....	18-22°

The writers find it more satisfactory to dissolve 0.75 grm. of the soaps in strong alcohol (97 to 98%) and to leave the solution to stand at a temperature of 20° C. Under these circumstances rape oil commences to precipitate in a granular form in 15 to 30 minutes, and 5 to 10% of rape oil in admixture with other fats produces a spongy gelatinous precipitate within 2 hours, while in the absence of rape oil no precipitate usually forms under 15 to 18 hours. As the results are dependent on the degree of dryness of the soaps and the strength of the alcohol employed it is more satisfactory to carry through the test with some oil, such as cottonseed oil, as a control. The test under these conditions is quite reliable.

To detect small quantities of cottonseed oil, the present revisers recommend that the Halphen test be carried out in sealed tubes as suggested by Steinmann, while for still smaller quantities (down to 1%) R. Marcille<sup>1</sup> proposes that the sealed tubes be heated in an oil bath at a temperature of 120° when 5 to 10% of cottonseed oil give a bright red colour within 12 minutes, and 1% a distinct red after 1 hour.<sup>2</sup> Attention is drawn to the fact that certain olive oils give a red colour when heated to 130° and for this reason care must be taken not to exceed 120° which temperature is stated not to produce any red colour with pure olive oil after 6 hours heating, though a slight yellow tint is usually observed.

"Saponified" olive oils are liable to be taken as adulterated with foreign oils on account of the different analytical figures which they give, and more particularly on account of the large precipitate which they yield when subjected to Bellier's test (see arachis oil). Archbutt<sup>3</sup> has investigated this point and has shown that one particular sample of oil of this type which contained 3.2% of unsaponifiable matter and gave a precipitate by Bellier's test, yielded no trace of arachidic acid by Renard's process and another sample which gave an unusually marked indication by Bellier's test, was found by Renard's method to contain less than 5% of arachis oil. Archbutt points out the necessity of a careful interpretation of this test and due confirmation by Renard's method before the presence of arachis oil be certified.

<sup>1</sup> *Ann. Falsific.*, 1910, 3, 235.

<sup>2</sup> Other proposed improvements in this test will be found under cotton oil, page 135.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1911, 30, 5.

Attention is drawn to the turbidity of these oils, which is usually due to the presence of moisture, and to the increased viscosity, together with various other analytical differences exemplified in the following table of analyses of nine samples examined by him.

Sp. gr. at 60° F.....	0.9167	0.9165	0.9175	0.9186	0.9169	0.9175	0.9169	0.9161	0.9179
Efflux time of 50 c.c. from Redwood's viscometer at 60° F. (seconds) .....	516.0	450.0	437.0	478.0	480.0	561.0	524.0	428.0	465.0
Saponification value.....	186.1	186.9	189.3	186.9	186.0	185.5	185.9	185.4	185.8
Free (oleic) acid.....	2.9	3.3	1.0	1.1	0.9	2.3	1.8	0.4	1.6
Iodine value.....	86.4	85.1	85.8	84.4	85.5	85.6	85.0	86.5	86.2
Unsaponifiable matter.....	2.49	2.34	2.08	2.70	3.30	3.32	3.23	2.98	2.67
Arachidic acid, by Renard's process .....									

"Extracted" olive oil, obtained by means of carbon disulphide, is liable to contain traces both of this solvent and of free sulphur. The latter may be detected by warming a silver coin or strip of copper in the oil. Carbon disulphide may be detected by the method suggested by E. Millau<sup>1</sup> who distils 50 grm. of the oil with 10 c.c. of pure amyl alcohol, collecting the first 5 c.c. of the distillate and to 4 c.c. of the distillate adds 1 c.c. of kapok or cottonseed oil together with a few mg. of sulphur, heating the mixture in a sealed tube for 1 hour.

The present revisers found that as little as 0.05% of carbon disulphide can be easily detected in this way. Olive oils which have been extracted by carbon disulphide have been examined by F. Canzoneri and G. Bianchini<sup>2</sup> who found them to differ from the ordinary expressed oil in the following respects:

- (1) High specific gravity.
- (2) Lower solidification of the fatty acids (*e.g.*, 17.5° to 19.7°).
- (3) Lower iodine value (77.5 to 80.2).
- (4) High acetyl value.
- (5) Lower refractive index (59° to 61° Zeiss) except in the case of oils bleached by oxidation, in which the reading exceeds 63°.
- (6) Saponification value lower than normal.

O. Klein<sup>3</sup> has examined 30 samples of oil prepared from known varieties of olives and 30 commercial samples from which he deduces the following limiting values for Portuguese oils:

	Sp. gr.	Refractive index (25° C).	Iodine value	Saponification value
Maximum.....	0.918	1.4682	85.0	195.0
Minimum.....	0.915	1.4660	75.0	185.0
Average.....	0.9168	1.4670	80.5	190.0

<sup>1</sup> *Ann. chim. anal.*, 1912, 17, 1.

<sup>2</sup> *Annali. Chim. Applic.*, 1914, 2, 1.

<sup>3</sup> *Chem. Zentr.*, 1912, 1, 1664.

TEA SEED OIL.

The following figures have been obtained by the present revisers for a sample of commercial oil obtained from Chinese tea seed.

Sp. gr. at 15.5°.....	0.9163
Iodine value.....	84.35
Refractive index at 40° C. (Zeiss).....	53.8
Saponification value.....	190.5
Free fatty acids (as oleic).....	1.84

Menon<sup>1</sup> has examined seeds from Upper Assam which on extraction with petroleum ether yielded 16.1% of an oil having the following characteristics:

<b>Oil:</b>	
Sp. gr., 15°/15°.....	0.9028
Saponification value.....	189.9
Reichert-Meissl value.....	0.56
Titration number of insoluble volatile acids.....	0.56
Iodine value.....	92.7
<b>Fatty acids:</b>	
Insoluble fatty acids + unsaponifiable.....	2.6
Insoluble fatty acids.....	93.04
Melting point.....	38.9°
Neutralisation value.....	199.9
Mean molecular weight.....	280.5
Iodine value.....	94.13

The fatty acids consisted of about 25% of solid acids melting at 57.8° and having a neutralisation value of 209.8, mean molecular weight 267.3, iodine value 13.84, and 74.75% of liquid acids of the neutralisation value 191.1, mean molecular weight 293.5, and iodine value 117.8.

MUSTARD OIL.

**Black Mustard Oil.**—The black seeds contain about 30% of oil, which is usually obtained as a by-product from the manufacture of mustard.

The Indian oil is often adulterated with sesame and similar oils.

**White Mustard Oil.**—The white seeds contain about 25% of oil. The following figures have been recorded by Grimme for the oil obtained from four different kinds of seeds.<sup>2</sup>

	Sinapis arvensis L.	Sinapis chinensis L.	Sinapis dissecta L.	Eruca sativa Lmk.
<b>Oil:</b>				
Sp. gr. at 15° C.....	0.9228	0.9230	0.9221	0.9198
Solidifying point.....	−13° to −15°	−14°	−13° to −14°	−8° to −10°
Saponification value.....	179.4	177.3	178.2	174.4
Iodine value.....	102.6	103.3	105.6	101.8
Refractive index at 20° C.....	1.4738	1.4736	1.4725	1.4723
<b>Fatty acids:</b>				
Fatty acids, per cent.....	94.21	94.28	94.34	94.24
Unsaponifiable matter, per cent...	1.12	0.96	0.96	1.07
Solidifying point.....	4–5°	14–15°	5–8°	8–10°
Melting point.....	6–8°	17–18°	9–10°	12–13°
Neutralisation value.....	179.8	182.0	181.7	180.1
Mean molecular weight.....	312.4	308.6	309.1	311.8
Iodine value.....	106.6	106.7	109.0	103.6
Refractive index at 20° C.....	1.4625	1.4648	1.4645	1.4643

<sup>1</sup> Year Book of Indian Guild of Science and Technology, 1912, 144.  
<sup>2</sup> Lewkowitsch, *Oils, Fats and Waxes*, 5th Ed., 2, 271.

The percentage of ethereal mustard oil obtained from the seeds of the above species are given in the following table:

Name	Ethereal mustard oil in seed, %	Ethereal mustard oil in extracted seed meal, %
<i>Sinapis arvensis</i> .....	0.959	1.308
<i>Sinapis chinensis</i> .....	1.407	2.022
<i>Sinapis dissecta</i> .....	0.833	1.150
<i>Eruca sativa</i> .....	1.075	1.586

A method for the estimation of essential oil of mustard is given in Abs. *J. Chem. Soc.*, 1912, ii, 308.

### COTTONSEED OIL.

Various improvements have been suggested in order to render the Halphen test still more delicate (some of these are described under olive oil). One of the most important and one which the present revisers have found to be extremely delicate, is the substitution of pyridine for amyl alcohol, as suggested by E. Gastaldi,<sup>1</sup> who carries out the test by mixing in a strong test-tube, 5 c.c. of the oil or fat to be tested, 1 drop of pyridine and 4 c.c. of carbon disulphide containing 1% of sulphur, corking the tube and heating in the water-bath for half an hour. As little as 0.25% of cottonseed oil will be found to produce a distinct red tint if compared with a control tube.

Utz<sup>2</sup> proposes to substitute pentachlorethane (b. p. 159°) for carbon disulphide so as to obtain a higher temperature, and states that he has obtained a reaction with 1% of cottonseed oil and that the colour is produced without the presence of amyl alcohol, if the temperature is sufficiently raised. Gastaldi and others, however (*vide* olive oil), have shown that if the temperature is raised appreciably above 120° a red colour is often produced when no cottonseed oil is present. The statement of Utz must therefore be accepted with due reserve.

### KAPOK OIL.

Known also under the name of Bastard cotton oil, is chiefly obtained from the seeds of *Eriodendron anfractuosum* which yields a fruit similar to that of the cotton plant, the chief distinction being that the seeds themselves are quite free from the hairs so characteristic of cotton seeds, and are small, round and black in colour—the hard shell constituting about 40% of the whole.<sup>3</sup> The tree abounds in Java, the West Indies, Africa, etc., where it is often termed the “silk cotton tree,” the same name being applied to the East Indian tree, *Bombax malabaricum*, which is very similar and from which kapok oil is also obtained, there being no commercial distinction

<sup>1</sup> Abs. *J. Soc. Chem. Ind.*, 1912, 31, 934.

<sup>2</sup> *Chem. Rev. Fett. Ind.*, 1913, 20, 291.

<sup>3</sup> Lewkowitsch.

drawn between the oils from these two sources. Sprinkmeyer and Diedrichs<sup>1</sup> have examined the oils obtained from the various species in order to differentiate between them if possible, and some of the figures which they have obtained are given in the following table.

Source	Java, E. Africa Ceylon, etc. <sup>2</sup>	Bombax malabaricum <sup>2</sup>	Mexican Bombax <sup>2</sup> (variety)	Commercial oil <sup>3</sup>
Sp. gr. at 15/15°.....	0.9235- 0.9326	0.9600	.....	0.9217
Ref. index at 40° (Zeiss).....	51.7 - 59.7	57.0	57.4	56.2
Iodine value.....	85.2 - 93.5	73.6	95.7	97.54
Acid value.....	18.5 - 21.02	3.0	12.62	15.0
Saponification value.....	189.2 - 194.5	194.3	192.8	192.5

Kapok oil is very like cottonseed oil in most respects and even gives the Halphen reaction to a slightly greater extent than the latter. Small quantities of kapok oil may, however, be detected in cottonseed oil by means of a modification of Becchi's test devised by Millau when applied in the form recommended by Durand and Band. The test is carried out as follows:

15 c.c. of the oil are saponified with sodium hydroxide and alcohol in the usual manner, 200 c.c. of boiling water are added and the whole boiled till the alcohol is evaporated. The fatty acids are then thrown out by the addition of *N*/10 sulphuric acid in slight excess. The fatty acids are skimmed off, and shaken twice with 15 c.c. of *cold* distilled water, the water being then drained off and the fatty acids dried rapidly in an oven at 105°. 5 c.c. of these fatty acids are shaken with 5 c.c. of a 1% solution of silver nitrate in absolute alcohol.

Under these circumstances cottonseed oil only produces a *barely perceptible brown colour*, while kapok oil rapidly develops a *deep coffee colouration*. By means of this test it is possible to recognise 1% of kapok oil in other liquid oils.

The imports of kapok seed to Holland and America are steadily increasing. The oil is used for the same purposes as cottonseed oil, with which it is often mixed, and increasing quantities are refined for edible purposes, more particularly in Holland.

The content of the oil in the whole seed ranges from 22% to, in some cases, 30%, while the kernels themselves usually contain about 40%. The seeds of *B. malabaricum* are generally rather higher in oil content.

## SESAME OIL.

Attention has been drawn by Zimmermann<sup>4</sup> to the failure of highly refined sesame oil to give many of the usual colour reactions, and he states that Solsein's stannous chloride test is the least affected. In the experience of the present revisers it is possible to obtain a strong Baudouin reaction

<sup>1</sup> *Zeit. Unters. Nahr. Genussm.*, 1913, 26, 86, and 450.

<sup>2</sup> Sprinkmeyer and Diedrichs (*Z. Unters. Nahr. Genussm.*, 1913, 26, 86 and 450).

<sup>3</sup> *Fatty Foods*, p. 222.

<sup>4</sup> *Mitt. d. k. k. Techn. Versuchsanst.*, 1912, 1, 71.



from the refined oil, though some processes of refining do, as stated above, considerably diminish the sensitiveness of this test. At one time the German regulations (see Vol. II, p. 141) required 10% of sesame oil to be added to all butter substitutes to facilitate their detection, but owing to the aforesaid reduction in the sensitiveness of the Baudouin reaction, it was necessary subsequently to modify these regulations, and to require such an amount of sesame oil to be added as would suffice to give a distinct red colour under specified standard conditions (Vol. II, p. 316) without laying down any limits as to the quantity of sesame oil which might be required to fulfil these conditions.

### SOJA-BEAN OIL.

The very large quantities of this oil which have come on the market in this country and more particularly in the U. S. A., render it of great commercial importance.

Many investigations have been carried out with the object of utilizing the oil for various purposes other than that of soap making and the recorded statements of different observers are most contradictory. This divergence of opinion may be explained by the great variety of different species of soja beans and it is hardly to be expected that they should all yield an oil having identically the same properties.

Maximilian Toch<sup>1</sup> has examined 33 different varieties of soja beans and he points out that in the records of the Department of Agriculture at Washington no less than 280 varieties of soja beans have been recorded. This investigator explains the controversial statements of other workers on the grounds that the oil from certain varieties of beans is suitable for use in paints (*i.e.*, as a substitute for linseed oil) and goes on to draw a favourable comparison between those types and linseed oil, pointing that the type of oil adapted for use in paint possesses two characteristics, (*a*) that when heated to 500° F. for a few minutes, it will become bleached and remain bleached, and in this respect resembles linseed oil to a certain extent; (*b*) that when heated to 500° F. and blown with dry air for 5 to 7 hours, it thickens in a similar manner to linseed oil and attains a sp. gr. of 0.960 or over. The following figures were obtained by this author for a standard sample of cold-pressed Manchurian bean oil, which was heated to 500° F. and after cooling to 300° F. blown vigorously for 7 hours.

	Sp. gr., 60° F.	Acid value	Iodine value
Original oil.....	0.929	2.6	133.6
Blown oil.....	0.963	1.9	105.6

Blown soja oil is used in linoleum manufacture. The figures given in the following table were obtained in Messrs. Toch Bros.' research laboratory.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1912, 31, 572.

Name	Colour of seed	Colour of oil	Sp. gr., 15° C.	Acid value	Iodine value
Meyer.....	Brown	.....	0.9264	0.44	127.0
Peking.....	Black	.....	0.9279	0.14	135.4
Haberlandt.....	{ Straw- yellow	Extremely pale.	0.9244	0.00	129.8
Farnham.....	{ Straw- yellow		0.9234	0.65	131.8
Taha.....	{ Black	Pale amber some- what deeper than than above.	0.9248	0.16	127.0
Mammoth.....	{ Olive		0.9222	0.47	118.2
	{ Saddle				
	{ Straw- yellow				
Edward.....	{ Straw- yellow	Med. amber.	0.9257	1.14	124.6
Shanghai.....	Black	{ Same depth as pre- vious olive tone.	0.9241	0.63	127.8
Refined linseed.....	.....	.....	0.933	1.0	180.1

Soja oil is used to a certain extent as an edible oil, but has not fulfilled anticipations, still while there is no difficulty in preparing a tasteless and odourless oil, it has been the experience of the present revisers that this does not keep very well, and has a tendency to develop an unpleasant "oxidised" taste.

CANDLE NUT OIL.

In addition to the seeds obtained from the South Sea Islands large quantities are exported from Hongkong and Fiji, as well as Australia and New Zealand.

The oil is known as "Kekune" or "Country Walnut oil," etc.

The seeds of *Aleurities triloba* are said to produce an edible oil, but that obtained from *Aleurities moluccana* has, as has been pointed out by Lewkowitsch, purging properties. The seeds from both varieties are sold indiscriminately under the names of "Candle nuts," "Baio nuts," "Lumbang nuts," etc.

The present revisers (*Fatty Foods*, page 251) have extracted samples of the oil from authentic specimens of the seed of both varieties and have obtained the following figures:

	Aleurities moluccana	Aleurities triloba <sup>1</sup>
Saponification value.....	190.3	202.5
Iodine value.....	164.0	143.8
Ref. index at 40° C. (Zeiss scale).....	65.7	61.8
Free fatty acids (as oleic).....	20.1 %	1.0 %

If these figures are compared and contrasted with those of other observers (*vide* Vol. II, 149) it would appear that the oil from *Aleurities triloba* has a higher saponification value and a lower iodine value than that of *Aleurities moluccana*.

A sharp distinction must be drawn between Candle nut oil and Tung oils,

<sup>1</sup> The oil remained liquid below zero without depositing "stearine."

though the Chinese variety of tung oil (*vide* page 140) is obtained from closely allied species of Aleurities (var. Fordii and Montana). Tung oils are decidedly poisonous.

HEMP SEED OIL.

Hemp seeds contain about 33-35% of oil.

The following figures were obtained by the revisers from one genuine sample :

Sp. gr. 15/15°.....	0.9283
Saponification value.....	191.0
Iodine value.....	161.7
Ref. index at 40° (Zeiss).....	73.5
Free fatty acids, per cent.....	2.3

PINE NUT OIL.

The data in the following table have been collected by Lewkowitsch.<sup>1</sup>

Oil from	Yield oil, %	Sp. gr. at 15°	Solidifying point	Saponi- fication value	Iodine value (Wijs)	Ref. index	Observer
<i>Pinus sylvestris</i> , L.....	32.1	0.9326	-28 to -29	189.8	147.1	1.4704 at 35°	Grimme.
<i>Pinus montana</i> , Mill.....	29.6	0.9318	-25 to -26	189.6	145.7	1.4698 at 35°	Grimme.
<i>Pinus cembra</i> , L.....	.....	0.930	-20	191.8	159.2	.....	v. Schmoelling.
<i>Pinus cembra</i> , L.....	35.7	0.9316	-20 to -21	188.0	156.3	1.4710 at 40°	Grimme.
<i>Pinus picea</i> , L.....	32.8	0.9268	-25 to -26	190.5	120.9	1.4879 at 35°	Grimme.
<i>Pinus abies</i> , L.....	31.6	0.9312	-26	192.0	120.5	1.4742 at 35°	Grimme.
<i>Pinus Gerardiana</i> , Wall..	30.7	0.9307	-17	191.3	120.9	1.4685 at 40°	Grimme.
<i>Pinus pinea</i> , L.....	21.8	0.9326	-22	192.6	118.3	1.4679 at 35°	Grimme.
<i>Cupressus sempervirens</i> } <i>v. horizontalis</i> , Mill.	10.8	0.9320	-4	188.6	135.1	1.4857 at 35°	Grimme.
<i>Thuja occidentalis</i> , L.....	15.0	0.9298	-8	186.7	154.8	1.4795 at 35°	Grimme.
<i>Pinus monophylla</i> .....	.....	0.933	.....	192.8	101.3	1.4769(?)	Blasdale.
<i>Pinus Fremontiana</i> .....	.....	.....	.....	189.0	108.0	1.4543 at 40°	Adams and Holmes.
<i>Pinus monophylla</i> .....	.....	.....	.....	.....	.....	.....	.....
<i>Pinus Fremontiana</i> .....	.....	.....	.....	.....	.....	.....	.....

POPPY SEED OIL.

The oils obtained from different varieties of poppy seed are divided commercially under two headings:

- (1) "*Huile d'œillette*," obtained from the grey or blue European seed.
  - (2) "*Huile de pavot*," from the brown or mottled seeds of foreign origin.
- "Huile d'œillette" is the better oil and commands a higher price.

The following simple test serves to distinguish the two types of oil.

The oil is violently shaken in a bottle when it will be found that (1) gives a fine emulsion of air bubbles, rendering the oil turbid, (2) behaves quite differently and does not give a fine emulsion nor is the froth so persistent.

"Huile d'œillette" possesses a much more golden-yellow colour than "huile de pavot," and so much so, that it is often necessary to colour the latter in order to render it saleable.<sup>2</sup>

SAFFLOWER OIL.

The oil is obtained from 2 distinct varieties, *Carthamus tinctorius* and *Carthamus oxyacantha* the latter being "wild" safflower. The seeds are

<sup>1</sup> Oils, Fats and Waxes, 5th Ed., Vol. 2, p. 141.  
<sup>2</sup> L. Vuastart, Ann. Patisf., 1909, 2, 276.

commonly known as "Kurdee" or "Kardai" seeds, and the quantities expressed are largely on the increase. The oil-cake produced, from the decorticated seed, contains nearly 50% of protein. The figures in the following table have been obtained by Leather.<sup>1</sup>

District	No. of samples	Oil, %	Wt. of 100 seeds in grm.
Central Provinces.....	6	23.54-31.82	3.405-6.774
Bombay Presidency.....	9	28.79-32.23	4.210-5.516
Madras Presidency.....	8	23.88-33.55	2.973-4.622
United Presidency.....	6	27.94-29.78	3.348-4.936
Bengal.....	1	22.47	3.209

The oil gives a marked hexabromide reaction and is a good drying oil being used by the natives in parts of India for linoleum manufacture.

### SUNFLOWER OIL.

This oil is usually obtained from the fruits of the *common* sunflower, and seldom from the seeds alone as is generally supposed. It should be noted that the portion usually termed "the seed" is really the whole fruit. The plant is indigenous to Mexico, but is extensively cultivated in Russia, China and Hungary and is so abundant in South Africa that it is used to mark out the boundaries of fields. Notwithstanding the fact that it is a very easy plant to grow and produces an enormous yield of fruits, the attempts to introduce it into India and the United States have not proved very satisfactory and the crop in Great Britain is too small to be of any commercial importance, though the climatic conditions lend themselves to its production. It appears that the value of the crop is not realised by the conservative British farmer.

Sunflower oil serves well for edible purposes though it is a little difficult to refine owing to its tendency to form emulsions.

The fruits vary in colour from white to a dark brownish black, and contain about 22-25% of oil (45-50% calculated on the true seed). The oil from the white fruits has been found by the present revisers to have a much lower iodine value (106) and a lower refractive index than that yielded by the black seeds.

### TUNG OILS.

**Chinese Wood Oil.**—The enormous increase in the use of this oil of late years has caused it to be the subject of many investigations, one of the chief objects in view being to arrive at some satisfactory method of assaying its purity, and to set up a standard specification for purpose of sale, to which all pure samples should conform. As might be expected, a number of quite useless tests have been put forward.

<sup>1</sup> *Mem. Depart. Agric., India, March, 1907.*

A general survey of the more important methods has been made by Chapman<sup>1</sup> whose paper should be consulted. He points out that the analytical determinations of the greatest importance are the sp. gr., the iodine value, the refractive index, the viscosity and the polymerisation test.

The Wijs method of determining the iodine value is recommended, if carried out in the following manner:

About 0.1 gm. of the oil is dissolved in 20 c.c. of purified carbon tetrachloride, 30 c.c. of the Wijs solution added and the absorption allowed to proceed for 3 hours in the dark.

In connection with the viscosity (time of efflux) the same author draws attention to the fact that the viscosity of tung oil is greater than that of any other fatty oil likely to be used as an adulterant, but the warning is added that the viscosity may be considerably increased by heating the oil to a temperature short of that required for solidification.

**Polymerisation Tests.**—A great number of the tests put forward are based on the property which this oil possesses of setting to a firm mass when heated. It has been suggested to solidify the oil by heating it under standard conditions and to grind and extract the mass with ether, but the present revisers have found this to be most misleading and unsatisfactory except in the case of gross adulteration which could be more easily detected by other methods.

In a circular issued by the New York Produce Exchange a method devised by C. V. Bacon is tentatively put forward.

"Into a test-tube  $\frac{3}{4}$  in. diameter and 4 in. in length there are transferred about 10 c.c. of pure China wood oil; into another test-tube there is transferred a similar volume of pure China wood oil adulterated to the extent of 10%. A sample of the oil to be tested is treated in a like manner, and these are placed in a proper support and immersed in an oil bath which has a temperature of about 288° C.; so that when the tubes are in it a temperature of 280° or 285° C. (maximum) can be maintained. The oil bath containing the tubes is maintained at this temperature for exactly 9 minutes, the tubes are then withdrawn and the test sample is compared with the pure oil, and with the same oil adulterated with 5 and 10% of foreign oil. After the tubes are withdrawn from the oil bath, each tube should be stabbed from top to bottom with a small bright spatula. Pure oil will give a hard, clean cut, and when the knife is withdrawn the incision will look like a straight line, but an oil having an adulteration as low as 5% will invariably be softer, and the incision will have a peculiar feathered effect; whilst an adulteration of 10% will be soft and "pushy," an adulteration exceeding 12% in many instances will remain entirely liquid."

A further test which is used by the New York importers and varnish makers is described as follows:

"Hankow and Shanghai wood oil, 100 gm., should be heated in an

<sup>1</sup> *Analyst*, 1912, 37, 543.

open basin (6 in. in diameter) as soon as possible to a temperature between 540° and 560° F. and if it solidifies in about 6 to 6½ minutes, cuts dry, and is firm in body, without discolouration and without being sticky, it should be passed as a good delivery. For Canton and Hongkong wood oil deliveries, the time should be from 4½ to 5½ minutes in an open basin as above. Should a longer time be taken by what is presumably pure wood oil, other tests confirming purity shall be positive.”

Chapman (*ibid.*) criticises these tests and as a result of considerable experience states that he attaches more importance to the hardness of the jelly obtained under standard conditions than the time required for bringing about polymerisation. He has devised the following method of carrying out the test, which he finds to be capable of yielding definite and concordant results:

In the following table he gives the results of the examination of 17 samples of Chinese wood oil from Hankow:

Sample	Iodine value	Sp. gr. 15°/15°	Saponification value	Ref. index at 20°	Time of efflux at 15.5°, seconds	Polymerisation 1 hour at 250°
No. 1.....	169.9	0.9419	196.6	1.5207	2,178	Very hard.
No. 2.....	168.4	0.9406	193.8	1.5181	1,636	Hard.
No. 3.....	166.5	0.9426	194.3	1.5190	1,946	Fairly hard.
No. 4.....	166.4	0.9417	193.0	1.5170	1,880	Fairly hard.
No. 5.....	168.8	0.9430	195.6	1.5195	2,017	Very hard.
No. 6.....	170.0	0.9440	194.5	1.5180	1,849	Hard.
No. 7.....	168.6	0.9416	193.0	1.5150	.....	Fairly hard.
No. 8.....	171.0	0.9414	192.0	1.5170	.....	Hard.
No. 9.....	169.7	0.9437	194.1	1.5176	1,997	Hard.
No. 10.....	173.0	0.9420	192.5	1.5165	1,722	Hard.
No. 11.....	176.2	0.9417	192.0	1.5168	1,605	Hard.
No. 12.....	172.6	0.9429	196.0	1.5180	1,740	Hard.
No. 13.....	174.2	0.9427	194.6	1.5182	1,690	Hard.
No. 14.....	173.7	0.9430	195.0	1.5194	1,820	Hard.
No. 15.....	172.8	0.9440	194.6	1.5193	2,047	Hard.
No. 16.....	169.5	0.9420	195.2	1.5160	1,804	Hard.
No. 17.....	169.6	0.9433	195.2	1.5187	1,820	Very hard.
Average.....	170.6	0.9425	194.2	1.5179	1,850	

The following extract has been taken from his paper:

“About 5 c.c. of the oil to be examined are introduced into each of 2 test-tubes 6 in. long by 5⁄8 in. diameter. These are then immersed in a bath containing melted paraffin wax at a temperature of approximately 100°. The temperature of the bath is then raised to 250°, taking about 15 minutes for the operation. As soon as that temperature is reached the time is noted, and the source of heat adjusted so that the temperature of the bath is maintained constant at 250°. At the end of half an hour one of the tubes is withdrawn, allowed to cool, and, when cold, is broken, and the jelly examined. The other tube is kept in the bath at 250° for a further period of half an hour, at the end of which time it also is withdrawn and allowed to cool; it is then broken, and the hardness of the jelly observed. Chinese wood oil of good quality should give at the end of half an hour a fairly firm jelly, which, at the end of 1 hour, should become quite hard. It is advisable in all cases to carry out comparison tests alongside of the oil under examination, using for the purpose a sample of oil known to be of good quality.

“I have not found it possible to express the hardness of the solidified cylinders by means of numbers, but with a little experience it is very easy to distinguish between a sample of



genuine oil and the same oil containing a small percentage of some fatty oil, such as soja bean or sesame. In referring to the polymerisation experiments, I have used the words "very hard," "hard," and "fairly hard," to denote the consistency of the polymerised oil, since such expressions are quite sufficient for the purpose. In addition to the degree of hardness of the solid cylinders of oil, some attention should be given to their physical characters. When cut with a knife or broken across, the cut or fractured surface should be smooth and free from stickiness, and small portions when rubbed in the hand should break down completely into a soft crumbly mass, which should not adhere to the fingers."

**Hexabromide Test.**—This test becomes of considerable importance for the detection of other oils which yield insoluble hexabromides, such as fish or marine animal oils as well as linseed, rubberseed oil, etc., for it has been shown by Hehner and Mitchell and independently by Jenkins and Chapman (the latter having worked on the 17 samples above referred to as well as on 4 samples of Japanese wood oil) that no insoluble hexabromides are obtained by the methods proposed by Hehner and Mitchell.<sup>1</sup> The present revisers have applied this test, as modified by Halphen,<sup>2</sup> to a large number of samples without obtaining a precipitate in any one case.

Candle nut oil (page 138) obtained from another species of *Aleurites* as well as perilla and hemp seed oils yield notable quantities of insoluble hexabromides.

Ware and Schumann,<sup>3</sup> give the following methods to detect adulterating oils, which is based on the insolubility of the potassium soaps of chinese wood oil in absolute alcohol. 3 grm. are saponified for 30 minutes under a reflux condenser with 100 c.c. of *N*/4 absolute alcoholic potassium hydroxide and the soap solution is cooled for 10 minutes at 0° and filtered through a Gooch crucible surrounded by ice. The precipitate is washed with ice-cold absolute alcohol previously saturated with the potassium soap of elæo-margaric acid and the residue dried *in vacuo* at 75° to 80°, in a current of hydrogen or carbon dioxide and weighed. The weight of the dry insoluble soap may be taken as measuring the wood oil in the sample.

Experiments on test samples containing from 5 to 40% of linseed and soja bean oils gave results within 1 to 2% of the theoretical.

	1	2	3
Sp. gr. 15.5°/15.5°.....	0.9406	0.9396	0.9276 to 0.9416
Ref. index at 25°.....	1.5143	1.5186	1.4790 to 1.5200
Moisture and volatile matter...	0.012 %	0.02 %	.....
Ash.....	0.0068 %	0.0026 %	.....
Acid value.....	3.45	0.90	0.2 to 0.8
Saponification value.....	192.27	193.02	188.2 to 192.4
Unsaponifiable matter.....	0.73 %	0.47 %	.....
Iodine value (Hubl, 18 hours) ..	169.3	169.6	151.6 to 171.7
Iodine-jelly test <sup>4</sup> .....	3 min. 37 sec.	4 min. 43 sec.	3 min. to 8 min.
Heating test <sup>5</sup> .....	9 min. 54 sec.	9 min. 23 sec.	10 min. to 11.5 min.

<sup>1</sup> *Analyst*, 1898, 23, 310.

<sup>2</sup> *Fatty Foods*, page 42.

<sup>3</sup> *Proc. Amer. Soc. Test. Mat.*, 1914.

<sup>4</sup> *Iodine-jelly Test.*—This test is carried out by mixing 1 grm. of the oil with 5 c.c. of chloroform at 25°, adding 5 c.c. of a saturated solution of iodine in the same solvent and stirring the mixture until a jelly is formed. The time is noted from the addition of the iodine to the formation of a jelly.

<sup>5</sup> *Heating Test.*—5 c.c. of the oil are placed in a test-tube containing a glass rod and heated in an oil-bath at 282°, the rod is raised after 9 minutes and afterwards at intervals of 50 seconds, the time being noted when a jelly is formed.



In a report of the same Society<sup>1</sup> the figures in the foregoing table are given for two samples of Chinese wood oil, No. 1, being commercially obtained from the exporter and No. 2 expressed in the laboratory from Chinese wood oil nuts.

In column 3 is a summary of the average results of 11 investigators upon 3 samples of tung oil pressed from American grown nuts.

Japanese Wood Oil.

With regard to the source of Japanese wood oil considerable divergence of opinion exists as to the exact botanical species from which it is obtained. While Lewkowitsch,<sup>2</sup> states that the oil is obtained from the fruits of *Elaeococca vernicia*, quoting Kametaka<sup>3</sup> and distinctly states that this tree differs from *Paulownia imperialis*, Chapman (supra) examined oil extracted by himself from the fruits of the latter plant and obtained values closely agreeing with samples of Japanese wood oil obtained from Japan. Later, however, Wilson<sup>4</sup> states that the seeds actually examined by Chapman were those of *Aleurites cordata* and not those of *Paulownia imperialis*. In view however of the fact that Chapman himself examined oil extracted in his own laboratory from the seeds of *A. cordata*, it seems difficult to make these statements harmonise.

In a private communication to the present revisers, Chapman states that the oil examined by him was prepared from seeds forwarded to him from an authentic source in Japan and from a district in which the oil was being commercially manufactured and he was informed that the seeds in question were obtained from *Paulownia imperialis* and he further states that the seeds in question were quite different from those of *Aleurites cordata* in his possession, one specimen of which had been received from the Imperial Institute. In view of these facts, the present revisers are of the opinion that Chapman's statement as to the botanical source of these seeds must be taken as correct, though whether *Paulownia imperialis* is to be considered a botanical synonym for *Aleurites cordata* must be left an open question.

Whatever may be the source of the oil, it undoubtedly differs from Chinese wood oil, more particularly with regard to its powers of polymerisation and the iodine value is distinctly lower.

The following figures have been obtained by Chapman:

Source	Wakasa	Idzumo	?	Paulownia imperialis
Iodine value.....	158.0	149.0	151.8	153.5
Sp. gr. 15/15°.....	0.9377	0.9400	0.9349	0.9351
Saponification value.....	195.2	193.4	196.3	193.5
Refractive index at 20°.....	1.5083	1.5052	1.5034	1.5050
Time of efflux at 15°, seconds.....	1230.0	1620.0	.....	.....
Polymerisation, 2 hours at 250°....	Soft.	Soft.	Very soft.	.....
Bromine thermal value (rise in degrees).†	.....	.....	.....	24.5

<sup>1</sup> 1914, 17, 38.  
<sup>2</sup> *Oils, Fats and Waxes*, 5th Ed., 2, 82.  
<sup>3</sup> *J. Coll. Sci. Imp. Univ. Tokyo*, 1908.  
<sup>4</sup> *Bull. Imp. Inst.*, 1913, 13, 441.

Lewkowitsch<sup>1</sup> has contrasted the polymerising powers of Chinese and Japanese wood oils in the following table:

	Japanese tung oil	Chinese tung oil	
		No. 1	No. 2
Original oil.....	0.93386	0.9412	0.9419
Heated rapidly in wide-mouthed flask to 213° (420° F.).	0.9649	0.9428	0.9432
Heated rapidly in wide-mouthed flask to 232° (450° F.).	0.9355	0.9445	0.9411
Heated rapidly in wide-mouthed flask to 250° (482° F.).	0.9477	0.9448	0.9504
Heated rapidly in wide-mouthed flask to 300° (572° F.).	.....	0.9592	Solidified to hard jelly.
Heated rapidly in wide-mouthed flask to 310° (590° F.).	0.9553	0.9638	.....
Heated rapidly in wide-mouthed flask to 320° (608° F.).	0.9650	0.9700	.....
Heated rapidly in wide-mouthed flask to 330° (626° F.).	0.9694	Solidified to a jelly.	.....
Heated rapidly in wide-mouthed flask to 340° (644° F.).	0.9760	.....	.....
Heated to 150° and kept there for 2 hours.....	Solidified to a soft jelly. 0.9477	0.9365	.....
		0.9363	0.9463

WALNUT OIL.

A. Fouchet<sup>2</sup> has extracted by means of cold petroleum ether a yellow oil from seeds of a cross between *Juglans niger* and *Juglans cinerea* the yield being 50%. The oil so obtained gave the following figures:

Sp. gr. at 12 /4° C.....	0.925
Ref. index (n) <sub>D</sub> at 22° C.....	1.4765
Critical temperature of solution in absolute alcohol.....	78.5° C.
[α] <sub>D</sub> .....	±0
Saponification value.....	191.0
Acid value.....	0.37
Iodine value.....	151.0
Acetyl value.....	11.0

The author states that the oil consisted mainly of the glycerides of stearic oleic, linoleic and linolenic acids, there being 70% of linoleic acid. *Juglans niger* is largely cultivated in North America, the oil from which is known as *pecan oil*.

The following figures were obtained by A. C. Deiler and G. S. Traps<sup>3</sup> for oil extracted from the seeds (kernels) by ether.

Sp. gr. at 15 /15° C.....	0.9184
Saponification value.....	198.0
Iodine value (Hubl's method).....	106.0
Reichert-Meissl value.....	2.2
Insoluble fatty acids + unsaponifiable.....	93.4

ALIZARIN OIL, TURKEY-RED OIL.

W. Herbig takes advantage of the fact that the potassium salts of ricinoleic and sulphoricinoleic acids are largely soluble in cold acetone and the sodium salts only sparingly soluble, to effect a practically quantitative separation from the neutral oil. He proceeds as follows: From 2 to 5 grm. of

<sup>1</sup> *Oils, Fats and Waxes*, 5th Ed., 2, 84.  
<sup>2</sup> *Bull. Sci. Pharmacol.*, 1912, 18, 529.  
<sup>3</sup> *Amer. Chem. J.*, 1910, 43, 90.  
<sup>4</sup> *Färb.-Zeit.*, 23, 169 and 194.

the oil, according to the water content determined by Fahrion's method<sup>1</sup> are neutralised with  $N/1$  or  $N/10$  alkali, evaporated to dryness on the water-bath and the residue dried by Fahrion's method (*loc. cit.*). The dried mass (which must not be overheated) is boiled with 4 successive portions (75 c.c. each) of anhydrous acetone, each extract being cooled with ice and decanted through a filter. The solution is evaporated, the residue of oil weighed and its acid and saponification values determined. The separated salts are readily soluble in hot water yielding a solution ranging from faint yellow to deep yellow ("monopol soap"). This solution is treated with boiling hydrochloric acid to liberate the combined sulphuric acid and fatty acids, the latter being subsequently extracted with ether and examined. From 66% ("monopol soap") to 77% (Turkey-red oil) of the total sulphuric acid was found in the salts insoluble in acetone.

The ratios between the percentages of acetone extract and fatty acids were: "monopol soap" 1.13; Turkey-red oils 1.45 and 1.78. The sum of water and total fat constituted about 90% of the samples of oil (84% in the case of "monopol soap"). This affords a practical sorting test.

### CROTON OIL.

It is of interest to note<sup>2</sup> that this oil entirely loses its physiological properties when subjected to the process of hydrogenation.

### BASSIA TALLOW.

**Bassia Longifolia and Bassia Latifolia.**—The seeds of *Bassia longifolia* and *Bassia latifolia* are very similar and are much confused not only on account of admixture in commercial samples but more especially because they are commonly known under the same names, such as "Mowrah," "Mohwrah," "Mahua" and "Illipe;" the latter name being also applied to a very large number of exotic fats and ceases to have any designative value.

The present revisers (see *Fatty Foods*, p. 183 *et seq.*) have endeavoured to draw some better line of distinction between the fats of this group and suggest that less confusion would arise if they were referred to as "Latifolia Fat" and "Longifolia Fat."

**Bassia Longifolia.**—Occurs in southern India *only*. The seeds are somewhat similar to those of *B. latifolia*, but as a general rule are slightly longer and narrower, but this does not hold true in every case.

The kernels which represent about  $\frac{3}{4}$  of the weight of the seed contain some 55% of fat.

In all probability the fat from these seeds yielded the original "Illipe butter."

**Bassia latifolia** occurs mainly in central India—from western Bengal to Burma—but does not extend to southern India. The seeds are rather more

<sup>1</sup> *J. Soc. Chem. Ind.*, 1913, 32, 1118.

<sup>2</sup> *Ber.*, 1909, 42, 1546.

round and shorter than those of *B. longifolia* and larger than those of *B. butyracea*. As in the case of *B. longifolia* the kernel represents  $\frac{3}{4}$  (or rather more) the weight of the seed and contains from 57–60% of fat.

**Bassia Butyracea.**—The seeds of *B. butyracea*, which occurs in the sub-Himalayan districts—from the Ganges to Bhutan—are very similar in appearance to *B. longifolia* and *B. latifolia* except that they are much smaller.

The fat obtained from the seeds is known as “Phulwa,” the name “Phulwara” being applied to the seeds only. The seeds contain some  $\frac{3}{4}$  of their weight of kernel, which kernel has a fat content of some 66%. This fat is one of the most common adulterants of Ghee and on this account has actually been given the name of “Ghee” in some text-books. The present revisers with a view to differentiating between the fats obtained from the three foregoing seeds examined samples of authentic origin and having extracted the fat themselves by means of petroleum ether, obtained the figures given in the following table:

Determination	<i>Bassia latifolia</i>	<i>Bassia longifolia</i>	<i>Bassia butyracea</i>
Ref. index at 40°C. (Zeiss butyro-refractometer.)	47.7	49.3	47.8
Iodine value (Wijs).....	59.4	62.6	42.6
Saponification value.....	192.2	189.8	188.2
Sp. gr., 99°/15C.....	0.8595	0.8624	.....
Free fatty acids (as oleic).....	24.6%	3.3%	8.74%
Unsaponifiable matter.....	.....	.....	1.36
Baryta value:			
(a) Total.....	263.0	258.2	257.3
(b) Insoluble.....	252.0	252.8	255.7
(c) Soluble.....	11.0	5.4	1.6
d = (200 + c).....	+41.0	+47.4	+54.1
Reichert-Meissl value.....	.....	.....	1.31
Polenske value.....	.....	.....	0.65

Shea butter or Karité butter is obtained from the seeds of *Butyrospermum* (or *Bassia*) *Parkii*, a tree largely grown in West Africa, French Soudan, etc. The general appearance of the seed is not unlike that of *B. longifolia*, *B. latifolia* and *B. butyrospermum*, though so very considerably larger in size as to render it impossible to be confused with these.

The whole seeds have a varying content of fat—amounting to 33 to 45% of its weight which is equal to 50–60% of the kernel, the latter being the portion usually imported.

Originally the fat found an outlet for the manufacture of soap and candles, but of late years, owing to improvements in the methods of de-odourising and refining, its uses as an edible fat in the form of a lard substitute or pastry fat has been very considerable. The “stearine” has been utilised to a limited extent as a chocolate fat and the “oleine” for baking purposes.

One of the disadvantages of its use for edible purposes was at one time its large content of unsaponifiable matter—(5–9%)—but manufacturers have now learned how to select seeds giving the lowest yield of unsaponi-

fiable matter, and methods of removing a proportion of the latter have come into use. The figures in the following tables were obtained by the present revisers.

SHEA NUT OIL.

Determination	Usual limits	Typical specimen
M. p., °C., incipient fusion.....	29° to 32°	.....
M. p. °C., complete fusion.....	37° to 42°	41.2°
Solidifying point, °C.....	25° to 30°	26.8°
Saponification value.....	180 to 190	186.9
Ref. index at 40° C. (Zeiss butyro-refractometer).....	55.5 to 56.5	56.3
Iodine value (Wijs).....	57 to 63	58.93
Sp. gr., 15°/15 C.....	.....	.....
Sp. gr., 99°/15 C.....	.....	.....
Free fatty acids (as oleic).....	2 % upwards	8.29 %
Unsaponifiable matter.....	5 to 9 %	7.56 %
M. p. of fatty acids, °C.....	.....	.....

Determination	Shea nut "stearine"	Shea nut "oleine"
M. p., °C., incipient fusion.....	40.0°	.....
M. p., °C., complete fusion.....	55.5°	.....
Solidifying point, °C.....	34.2°	24.0°
Saponification value.....	179.7	181.6
Ref. index at 40° C. (Zeiss butyro-refractometer).....	52.7	58.7
Iodine value.....	51.9	62.3
Free fatty acids.....	3.4 %	5.89 %
Unsaponifiable matter.....	0.25 %	7.72 %
Reichert-Meissl value.....	.....	2.60
Polenske value.....	.....	0.72

**Bassia Taxisperma** (Mimusops Djave), the seeds of which are commonly known as "Njave" or "Djave" being the "mahogany nuts" of the Gold Coast Colony.

The nuts are about 2½-3 in. long and 1¼ broad, having a bright polished mahogany coloured shell and a long oval hilum on one side. They are similar to, though rather larger and more pointed at the extremities than, Shea nuts. They contain about half their weight of a kernel in which there is 65 to 70% of fat.

As far as the present revisers are aware the fat has not been used for edible purposes and this is due to the fact that it usually contains traces of hydrocyanic acid produced by the enzymic decomposition of the non-fatty portion. It would be a comparatively easy matter to free the fat from this poison and in the event of no other unwholesome substance revealing itself, there seems to be no reason why this fat should not find a use for dietetic purposes.

The following figures have been obtained on a sample of the oil extracted from the seeds with petroleum ether by the present revisers.

Solidifying point.....	21.0°
Saponification.....	184.2
Ref. index at 40° C. (Zeiss scale).....	51.8°
Iodine value (Wijs).....	65.1
Sp. gr. 99°/15.....	0.8578
Free fatty acids (as oleic), %.....	9.27
Unsaponifiable matter, %.....	3.86
M. p. of fatty acids.....	52.8°
Solidifying point of fatty acids.....	47.8°

**Bassia Mottleyana**, Nat. Ord. Sapotaceæ.

The seeds, which are also known as katio, katiau, ketzian and by various other names, are like those of *B. latifolia* but very much smaller. According to Brooks<sup>1</sup> the tree grows abundantly in the swamps of Sadong and Saribas Districts. This author states that they are at present of no commercial value, but are highly prized by the natives for cooking and other purposes.

The average figures of a Dyak prepared oil are given in the table below. This oil had a bright yellow colour, sweet taste and pleasant odour of almonds.

Brooks has found the kernels to contain 47.5% of oil, while another sample examined by the present revisers had a fat content of 56%, and the proportion of kernel amounted to 75% of the weight of the whole seed, 100 of which weighed 30 grm.

Brooks describes the Dyak prepared oil as having a pleasant odour of almonds, which neither the Imperial Institute nor the present revisers have found to be true of oils which were extracted from the seeds in the laboratory. The native prepared fat was, however, found to have a pronounced smell of almonds and this was investigated by the Imperial Institute who found no prussic acid, but proved the presence of benzaldehyde, which they suggest had been added for the purpose of flavouring or scenting the oil.

## OIL FROM BASSIA MOTTLEYANA.

Description of sample	Dyak or native make			Extracted from seeds	
Observer	Brooks	Present revisers	Imperial Institute	Imperial Institute	Present revisers
Solidifying point.....	14.0	15.0	.....	.....	.....
Acid value.....	1.8	1.7	2.3	77.9	13.8
Sp. gr., 15°/15°.....	0.917	0.9174	.....	.....	.....
Sp. gr., 100°/15.5°.....	.....	.....	0.864	0.885	.....
Iodine value.....	63.2	66.5	65.0	65.0	65.2
Ref. index.....	53.4	.....	.....	.....	52.3
Saponification value.....	189.5	188.9	191.5	191.0	192.1
Unsaponifiable matter.....	0.41	.....	.....	.....	.....
Reichert-Meissl value.....	.....	.....	0.6	0.8	.....
Titer test.....	.....	.....	36.3°	36.4°	.....

## BORNEO TALLOW.

During recent years very large quantities of Borneo tallow have found their way on to the European market in the form of cacao-butter substitutes, the fat being obtained from various kinds of *Shorea*, chiefly *Shorea stenoptera*, *Shorea ghysbertiana*, *Shorea aptera* and *Shorea robusta* as well as *Isoptera borneensis* and species of *Hopea*. The seeds are usually sent into this country under the name of "Pontianak illipé nuts," being distinguished by the prefix

<sup>1</sup>Analyst, 1909, 34, 207.



"large" or "small" this not conveying any botanical distinction, but being purely a commercial differentiation of the dimensions of the seed.

The cacao-butter substitute is commercially known as "green butter," but it must be carefully borne in mind that this name also includes the fat of a number of similar exotic nuts.

The fat obtained from certain of these seeds is so similar in physical and analytical properties to true cacao butter that the problem of distinguishing it from cacao butter is of the highest difficulty. Various tests have been put forward with the object of detecting its presence, one of the most important having been suggested by Halphen.<sup>1</sup> His test has been investigated by the present revisers<sup>2</sup> who not having found it altogether satisfactory, have modified it in the following manner: 1 grm. of the clear filtered fat is dissolved in 2 c.c. of a mixture of equal parts of carbon tetrachloride and petroleum ether (distilling below 40°), and 2 c.c. of this solution are placed in a test-tube about 6 in. long and  $\frac{1}{4}$  in. in diameter. The tube is cooled in water and a solution of bromine in an equal volume of carbon tetrachloride added drop by drop, with constant shaking, until the colour of the bromine is permanent. The greatest care must be taken that only 1 drop in excess is allowed. The tube is then corked and allowed to stand. If, after the expiration of 15 minutes, the solution is perfectly clear, cacao butter is not present, or there is less than 10%. If the solution shows any turbidity, the presence of cacao butter is indicated, except in the case of one—somewhat rare—cacao butter substitute obtained from a species of *Guttanut*. This one exception, however, does not give quite the same turbidity as cacao butter, and can easily be distinguished as described below.

The method can be made roughly quantitative by making mixtures of cacao butter and some solid fat of low iodine value (such as cocoanut oil or cocoanut "stearine" if an actual "green butter" is not to hand), and comparing the turbidities produced by these mixtures and the sample under examination.

After the turbidity has been compared, 2 c.c. of petroleum ether are added to the tubes, which, after mixing by inversion, are allowed to stand all night, when the cacao-butter turbidity settles out as a very fine canary-coloured precipitate, easily distinguished from the slight flocculent precipitate which "green butters" under these circumstances usually throw down. It is to be also noted that cacao butter is completely soluble in the carbon tetrachloride-petroleum-ether mixture in the strength given above, whereas "green butters" usually become turbid almost immediately, and on standing for 2 hours usually throw down a considerable precipitate. Care must therefore be taken that the solution used for the test is quite clear.

The fat mentioned above, which might possibly be mistaken for cacao butter, may be distinguished from true cacao butter as follows: The solution

<sup>1</sup> *J. Pharm. Chim.*, 1908, 28, 345.

<sup>2</sup> *Analyst*, 1913, 38, 201.



of the fat, after treatment with the bromine, is allowed to stand for 15 minutes, and the turbidity is then carefully examined by transmitted light. The turbidity due to cacao butter is absolutely non-flocculent, and any appearance of flocculent particles is characteristic of the other fat. If now to the brominated solution are added 2 c.c. of petroleum (fraction of motor spirit distilling between 90° and 100° C.) and the whole mixed, any turbidity due to cacao butter entirely dissolves, whilst the turbidity due to this other fat remains quite insoluble.

By this means 5% of this fat may be detected in admixture with 95% of cacao butter or "green butter." More than 10% of this fat produces such a heavy flocculent precipitate that it could not possibly be mistaken.

Since this test was put forward difficulties have arisen in that many of the commercial products now often contain proportions of *hydrogenised* fats which considerably mask, and in some cases, vitiate the test.

#### ERRATA AND ADDENDA TO VOL. II.

Page 91, line 4 from bottom; H. Meyer and D. Beer<sup>1</sup> state that stearic and hypogæic acids are not present and that they have found the fatty acid of high melting point isolated by Hehner and Mitchell to be a mixture of arachidic and lignoceric acids.

Page 105, the section on apricot-kernel oil should commence "see also pp. 44 and 69."

Page 119, footnote 2, add "Chemist and Druggist, 1901, Sept. 21.

Page 176, cacao-butter section should commence "see also this volume, p. 71, and Vol. VI, p. 715.

Page 177, line 10, "30" should be "30°."

Page 180, at head of right-hand column, the o in front of degree sign should be deleted.

Page 188, at end of second paragraph there should be a reference to a new footnote as follows:

"Elsdon (*Analyst*, 1912, 38, 8) by the method of alcoholysis concludes that the composition of the mixed fatty acids is approximately as follows: caproic acid, 2%; caprylic acid, 9%; capric acid, 10%; lauric acid, 45%; myristic acid, 20%; palmitic acid, 7%; stearic acid, 5%; oleic acid, 2%."

Page 194, footnote 2 should be at the bottom of page 193, and the reference figure 2 should be inserted in the text after "Mitchell" in line 8 from bottom of page 193.

Page 217, line 9 from bottom, the second "or" should read "of."

Page 226, last line, "191.4" should read "196.2."

Page 231, in columns 8 and 14, the figures 5.60 and 65.92 opposite "R.-M. value" should be opposite "Reichert value."

Page 246, the words in brackets, lines 10 to 7 from bottom, should have been a footnote. There should be a comma after "410" and the semicolon after the second bracket should be omitted.

Page 252, the first footnote should be numbered 1.

Page 257, insert a new paragraph:

*Paraffin wax*, if present to the amount of 3% or more, can be easily detected by saponifying 5 grm. of the sample with alcoholic potassium hydroxide as in determining the saponification value and keeping the liquid hot on the water-bath in a corked flask. The paraffin will be seen floating on the surface of the liquid or adhering in small globules to the sides of the flask and the solution when diluted with hot water will be turbid. Genuine beeswax gives a clear solution

<sup>1</sup> *Monatsh.*, 1913, 34, 1195.

# BUTTER FAT.

By CECIL REVIS AND E. R. BOLTON.

## COMPOSITION OF BUTTER FAT.

Siegfield<sup>1</sup> has carried out some work on the acids present in butter fat and is of the opinion that the non-volatile acids consist of oleic, palmitic and myristic acids, a considerable quantity of the latter being sometimes present. Stearic acid was not found. The volatile acids consist chiefly of butyric, caproic and caprylic acids in very variable proportions, while the volatile insoluble acids contain a small quantity of caprylic acid and probably traces of palmitic and myristic acids. According to v. Fodor<sup>2</sup> caproic acid is the normal acid and not the isobutylacetic acid; this is confirmed by Smedley,<sup>3</sup> but the latter investigator finds 10 to 15% of stearic acid which is very improbable.

**Content of Volatile Fatty Acids, Soluble and Insoluble in Water** (Compare Vol. II, p. 283).—The Reichert-Meissl-Polenske method has been extended by the writers to work in connection with the method of Kirschner. The full process will be found under *Margarine*, page 166. As was pointed out by Kirschner and confirmed by the writers, this latter value is practically a measure of the butyric acid present and consequently gives a more sensitive indication for the detection of coconut oil than the Polenske value alone. The writers have suggested the following comparative values:

Kirschner value	Polenske value
20	1.6
22	2.1
24	2.6
26	3.2

These figures have been confirmed by Cranfield,<sup>4</sup> who has determined the R. M. Pol. & K. values for a large number of butters.

A variation of 1.0 must be allowed either way in the Polenske value corresponding to any particular Kirschner value, the addition of less than 5% of coconut oil causing the Polenske value to fall outside this limit.

A long and searching investigation of the variations in the Reichert-Meissl and Polenske figures for the butter fat of single cows over the whole period of lactation has been carried out by Beerbohm.<sup>5</sup> It appears that,

<sup>1</sup> *Zeit. Unters. Nahr. Genussm.* 1912, 24, 45.

<sup>2</sup> *Ibid.*, 1913, 26, 641.

<sup>3</sup> *Biochem. J.*, 1912, 6, 451.

<sup>4</sup> *Analyst*, 1915, 40, 439.

<sup>5</sup> *Milch. Zentr.*, 1913, 42, 513.

in general, the Reichert-Meissl figure falls during lactation, whilst the Polenske figure rises. The curves and tables given are very interesting, but are too lengthy for reproduction here.

According to Sunberg,<sup>1</sup> the percentage of coconut oil may be calculated from the tables given by Polenske<sup>2</sup> by taking the percentage there given, as percentages referred to the actual butter fat concurrently present and then calculating the percentage on the mixed fat. For instance, if the Polenske figure obtained gives from Polenske's tables 27%, then the actual percentage present in the mixture would be given by  $\frac{27 \times 100}{100 + 27} = 21.5\%$ .

The question of the likelihood of obtaining butter fat apparently adulterated with coconut oil, from cows fed on coconut-oil cake, has been investigated by Ledent,<sup>3</sup> whose results appear to show that the butter fat in such cases does give indications of the presence of coconut oil. This opinion has been confirmed by Barthel and Soden,<sup>4</sup> who show that it is not only the case with coconut-oil cake, but also with that of beet-root leaves. The writers are of the opinion that while this may occur occasionally in practice, it has not come under their notice in samples of butter representing the chief supplies of the English market. Should this adulteration with coconut oil be suspected, it could be confirmed by the phytosteryl acetate test, which would give positive results for the presence of phytosterol if the recrystallisation is carried out sufficiently often.

**The Method of Avé Lallemand** (Compare Vol. II, p. 288).—This method has been used by the writers since the time of its publication and there seems little doubt as to its value.

The following are a selection of figures obtained by them with different butters:

Butter	Total Ba	Insoluble Ba	Soluble Ba	Difference	R.M. No.	Polenske No.	Kirschner No.
Danish.....	315.90	252.95	62.95	— 10.00	29.7	2.7	24.2
	308.59	251.18	57.41	— 6.23	30.6	2.7	23.8
	310.38	253.31	57.07	— 3.76	30.2	1.9	23.8
	314.38	254.19	60.19	— 6.00	31.8	2.9	22.8
	312.03	254.30	57.73	— 3.43	30.1	1.8	21.4
	312.18	252.98	59.20	— 6.22	30.4	2.4	21.4
	317.66	256.04	61.62	— 5.58	31.8	3.0	20.9
	316.19	254.95	61.24	— 6.29	30.9	2.9	.....
	317.52	255.90	61.62	— 5.72	29.1	3.0	.....
	312.78	252.24	60.54	— 8.30	31.4	2.3	.....
English.....	313.16	253.18	59.98	— 6.80	30.1	2.3	24.6
	312.71	252.98	59.73	— 6.75	29.8	2.4	21.9
	312.04	253.57	58.47	— 4.90	30.1	2.5	21.9
	314.38	255.35	59.03	— 3.68	28.3	2.1	20.1
	312.26	251.61	60.65	— 9.04	31.4	2.4	22.9
	312.88	255.42	57.46	— 2.04	29.8	2.4	.....
	313.46	254.44	59.02	— 4.58	28.5	2.4	.....

<sup>1</sup> *Zeit. Unters. Nahr. Genussm.*, 1913, 26, 422.  
<sup>2</sup> *Arbeit Kaiserlich Gesundheitsamte*, 1904, 5, 45.  
<sup>3</sup> *Bull. Soc. Chim. Belge.*, 1913, 27, 325.  
<sup>4</sup> *Zeit. Unters. Nahr. Genussm.*, 1914, 27, 439.

Butter	Total Ba	Insoluble Ba	Soluble Ba	Difference	R.M. No.	Polenske No.	Kirschner No.
New Zealand.....	309.78	251.40	58.38	— 6.98	30.5	2.2	23.1
	316.90	251.86	65.04	— 13.18	32.7	2.7	24.7
	311.11	252.03	59.08	— 7.05	31.8	2.2	22.0
	317.59	253.87	63.72	— 9.85	29.6	3.3	.....
	313.41	252.91	60.50	— 7.59	32.4	2.7	.....
	318.70	254.50	64.20	— 9.70	32.2	3.0	.....
	316.25	254.15	62.10	— 7.95	32.4	2.6	.....
Irish.....	315.83	256.23	59.60	— 3.37	32.2	2.8	.....
	314.68	254.03	60.65	— 0.62	31.4	2.5	.....
	311.41	254.24	57.17	— 2.93	28.1	2.1	.....
	309.05	251.55	57.50	— 5.95	27.4	2.3	19.2
Normandy.....	316.43	253.90	62.53	— 8.63	32.4	3.2	.....
	316.26	252.52	63.74	— 11.22	31.9	3.0	.....
	311.94	254.95	56.99	— 2.04	28.8	2.1	.....
	316.96	256.73	60.23	— 3.50	31.4	2.9	.....
Probably adulterated..	312.75	258.17	54.58	+ 3.59	28.5	2.3	.....
	307.22	256.30	50.92	+ 5.38	26.6	1.8	.....
	309.13	257.89	51.24	+ 6.65	27.1	2.1	.....
	303.06	255.48	47.58	+ 7.90	24.6	1.7	.....

The above figures illustrate the type of result obtained. There is a great similarity in butter from different sources, and in the case of butters arriving from a known source, the method is of the greatest value. In many cases in which a positive result was obtained indirect evidence was forthcoming to support the analytical data.

It is necessary again to point out that the greatest care must be exercised in the analytical technique, more particularly in the original saponification titration, which must be obtained to the nearest half drop.

### Qualitative Tests.

**The Foam Test** (Compare Vol. II, p. 299).—This test, originally supposed to be of use in distinguishing between butter and margarine, has lost much of its value on account of the additions now made to margarine in order to bring about “browning” and “foaming” which are considered so essential in ordinary culinary operations. These compounds generally consist of some compound of casein together with sugar, and egg yolk is also used for the same purpose.

**Halphen's Test.**—This test has been improved by Gastaldi<sup>1</sup> by substituting pyridine for the amyl alcohol employed.

The modified test is carried out as follows: To 5 c.c. of the oil add 1 drop of pyridine, shake well and after adding 4 c.c. of carbon disulphide, containing 1% sulphur, heat for 20 minutes in the water-bath, the tubes being closely stoppered. The writers can confirm the value and greater sensitiveness of the test; they find it possible to detect at least 0.2% of ordinary cotton-seed oil products. It must be remembered that hydrogenation (see pages 122 and 173) partly destroys the chromogenetic substance responsible for the

<sup>1</sup> Abs. *J. Chem. Soc. Ind.*, 1912, 31, 934.

reaction, and for this reason the greatest possible sensitiveness that can be obtained for this test is desirable.

Utz has suggested the use of pentachlorethane (b. p.  $159^{\circ}$  C.) as solvent for the sulphur. The tubes can then be heated at a temperature nearly that of the boiling point of the solvent. It is stated that the test is rendered more delicate, but the writers have not as yet had experience of the method. (See Cottonseed Oil, p. 135.)

**Water** (Compare Vol. II, p. 304).—There has been a marked tendency of late years for the water content of butter to approximate to 16%. This is shown by the following successive figures obtained for various butters:

*Denish.*

15.8, 14.9, 16.2, 15.6, 15.8, 15.9, 15.7, 15.7, 15.7, 15.9, 15.1, 15.8, 15.5, 14.6, 15.0,  
15.3, 15.4.

*Blend 1.*

15.0, 14.0, 15.3, 15.2, 14.7, 15.3, 15.9, 15.3, 14.7, 15.7, 15.3, 15.9, 15.6, 15.4, 15.7.

*Blend 2.*

15.0, 15.7, 15.2, 16.1, 15.8, 16.4, 15.9, 15.4, 16.7, 15.9, 16.5, 15.9, 14.6, 15.9, 15.8,  
14.9, 15.9.

*English (country made).*

14.6, 14.9, 14.1, 14.2, 14.4, 14.5, 13.5, 14.7, 14.3, 15.4, 15.3, 15.4, 14.2, 13.8, 14.0, .  
14.2.

*Irish.*

14.0, 14.0, 13.7, 14.4, 13.8, 13.6, 13.9, 13.6.

The difference between the last two which do not compete on so keen a market, and the first three which do so compete, is very noticeable.

A few methods for the rapid estimation of water in butter have been devised for factory work, but it is probable that the ordinary direct drying method is really the simplest, though for obvious reasons the time required is not possible in factories where blending is going on, and the percentage of water is required while the butter is passing the blenders.

The method of Patrick (Vol. II, p. 306) is probably the most expeditious; it is quite satisfactory, but requires some little skill and attention to hit the exact point when all the water has gone and decomposition of the curd has not commenced.

For this reason distillation methods have been introduced which are rapid and quite accurate enough for the purpose.

(1) **Gray's Method** (*U. S. Dept. of Agric., Bureau of Animal Industry, Circ. 100*).

**Apparatus.**—The apparatus required for the test is as follows:

**Balance.**—Sensitive to 0.025 gm.

**Pipette.**—For measuring 6 c.c.

**Paper.**—Parchment, 5 by 5 in.; must be perfectly dry.

**Special Apparatus.**—As shown in figure. Referring to Fig. 6, *A* is a flask of capacity of a little over 70 c.c. *C* is a graduated tube, which is connected with flask *A* by means of a rubber stopper. *F* is a glass stopper ground into the tube *C*. The tube *C* is graduated after this glass stopper *F* has been ground in, the zero mark being the end of the stopper. Each mark of the graduation represents 0.02 c.c., or when a 10-grm. sample of butter is used each mark represents 0.2% of water. *E* is a glass condensing

jacket connected to the graduated tube *C* by rubber stopper *D*, as shown in the figure.

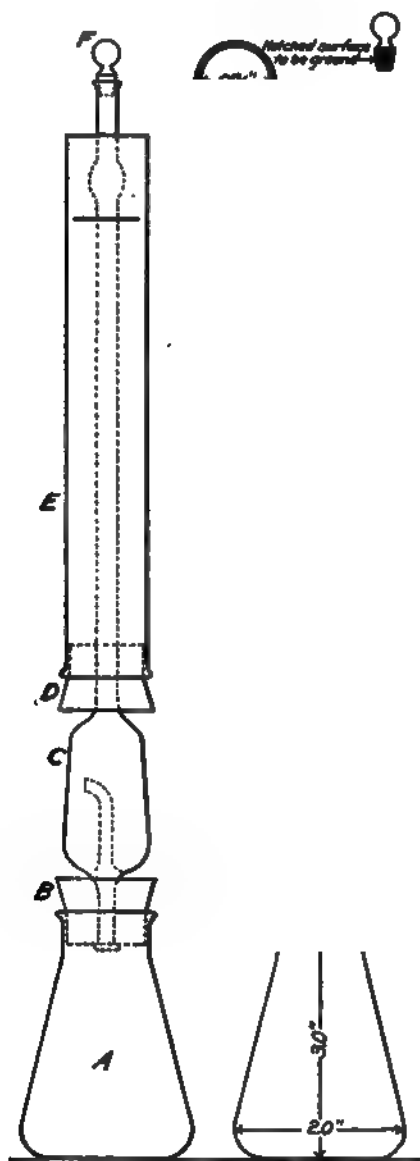


FIG. 6.

**Amyl Reagent.**—A mixture of amyl acetate (5 parts) and amyl valerate (1 part). Must be free from water soluble impurities in order to give accurate results.

### Method.

**Preparing the Sample.**—The sample of butter is placed in a suitable container (1 pint jar or metal cup will be satisfactory), and the latter immersed in water at about 100° F. The butter is stirred with a spatula or spoon until it has the consistency of thick cream and no free water can be seen. Samples of butter should not be left standing in open containers any length of time before making the water determination, as some of the water will evaporate and the percentage of water found finally will be too low.

**Weighing the Sample.**—Place on each pan of the balance one sheet of parchment paper and balance accurately. Place the 10 gm. weight on one pan and balance again by placing butter on the parchment paper on the opposite pan, placing the sample as near the centre of the paper as possible.

When exactly 10 gm. are weighed out remove the sample from the pan, and fold it in the parchment paper in such a way that the paper and butter may be slipped into flask *A*. Add 6 c.c. of the amyl reagent to the butter in the flask, connect the apparatus as shown in the figure and fill the condensing jacket *E* with cool water to within 1 in. of the top. Remove the stopper *F*.

Place the apparatus over the flame of the burner, applying heat to the bottom of the flask *A*. In a short time the butter will melt, running from the parchment paper into the amyl reagent. The water in the sample then boils and passes as steam into the tube *C*, where it is condensed and trapped. Watch the condensation in the graduated part of the tube *C*, and do not let the steam get higher than the 15% mark. If it goes higher than this, remove the flame, as there is danger of water being lost. If there is any indication of the mixture in the flask *A* foaming over, remove the flame. Foaming is usually prevented by 6 c.c. of amyl reagent, but some samples of butter, especially those of high moisture, require a trifle more than 6 c.c. In case of continued foaming, allow the mixture in the flask to cool, and add about 2 c.c. of the amyl reagent, and continue heating. After the water in the sample has boiled out, the temperature rises and the amyl reagent boils, driving the last traces of water and water-vapour from the flask and bottom of the stopper. Some of the amyl reagent is carried into the tube *C* with the steam, and some is boiled over after the water has been driven off. This amyl reagent in the tube is no disadvantage. The time required to expel all the water from the sample is not less than 5 minutes and with most samples need not be more than 8 minutes. When the mixture in the flask becomes brown and all the crackling in boiling ceases, it is safe to conclude that all water has been driven from the flask. Disconnect the flask *A* from the stopper *B*, place the glass stopper *F* in the tube *C*, giving it a slight turn to ensure its being held firmly, invert the tube *C*, first being sure that the mouth of the small tube inside the bulb is held up-



wards; pour the water from the condensing jacket *E*, after which the jacket may be removed. When the tube *C* is inverted the water and amyl reagent flow into the graduated part of the tube. To separate these and to get the last traces of water into the graduated part, the tube *C* is held with the bulb in the palm of the hand and the stoppered end away from the body, raised to a horizontal position, and swung at arm's length sharply down to the side. This is repeated a number of times until the dividing line between the water and the amyl reagent is very distinct and no amyl reagent can be seen with the water and *vice versa*. The tube should then be held a short time with the stoppered end downwards and the amyl reagent in the bulb of the tube agitated in order to rinse down any water that may be adhering to the sides of the bulb. The reading should not be taken until the tube and its contents have cooled so that very little warmth is felt. The water is in the bottom of the tube, and when a 10-grm. sample is taken the percentage may be read directly. Read the lower part of the meniscus.

The following method has been devised to estimate fat and salt in butter, particularly in creameries.<sup>1</sup>

**Estimation of Fat: Apparatus Required.**—A centrifuge.

A special separating funnel.

A balance which is sensitive to 0.01 grm. (A torsion balance such as is used in the moisture test is satisfactory if it is in good condition.)

An accurate set of metric weights.

A 10 c.c. graduated glass cylinder.

A 100 c.c. glass beaker.

**Special Separating Funnel.**—This is essentially a separating funnel with a capillary stem. The capacity of the funnel should be about 75 c.c. and its weight when empty should not exceed 70 grm. The stopper may be dispensed with if desired. It is a convenience in the final weighing, but not a necessity. Fig. 7 shows the form and dimensions of the funnel.

**Special Socket.**—This is a double socket for holding the above funnel while centrifuging, and is made of heavy sheet copper with hangers of steel. Each socket will hold 2 funnels. The cut shows the construction and dimensions. It differs in no material way from the socket ordinarily used on the Babcock centrifuge, except for the opening in the side. If the dimensions given fail to fit the centrifuge at hand, they may be changed to suit so long as the dimensions of the barrels are not altered. Care must be taken that the capillary stem of the funnel does not project far enough through the hole in the socket to strike against the side of the centrifuge when being whirled. It is best to fit a disc of rubber to the bottom of the socket.

**Sampling the Butter.**—In estimating fat in butter, great care must be taken in securing a representative sample and in preparing this for the test.

<sup>1</sup> Shaw, U. S. Dept. of Agric. Bureau of Animal Industry, Circ. 202, May 20, 1912. (Compare Vol. II, p. 306.)

Errors introduced by improper sampling are far greater than those in the actual test.

Samples are best taken with a butter trier, and one should always take several plugs from different parts of the tub or churn. These are placed in a suitable container, such as a 1-pint preserve jar or a cup, which is placed in water at about 100° F. The sample is then mixed with a spatula or spoon until about the consistency of thick cream. The sample must not be left

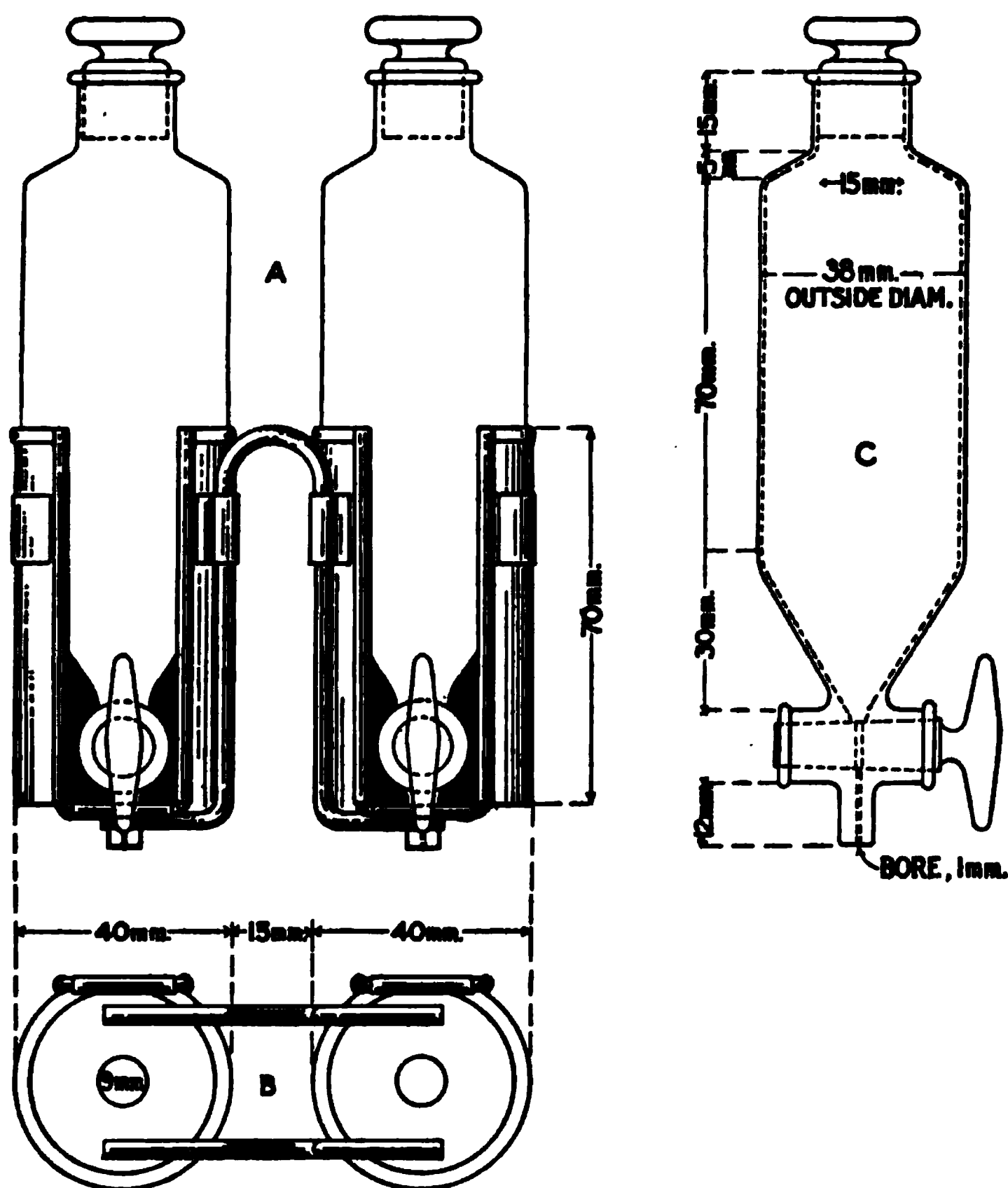


FIG. 7.—The special apparatus for estimating fat and salt in butter. A, the socket with funnels in position; B, view of socket from below; C, the separating funnel with capillary stem. (Reduced one-half.)

any length of time in open containers, since some of the moisture will evaporate. Should the sample be kept for any reason for a day or two before it is mixed, it should be placed in warm water (with the cover on the container) until melted, and then cooled while being previously shaken until it solidifies. The reason for this is that on standing some of the water will ooze out and

cannot be reincorporated except by emulsifying and cooling while in this condition. Too much stress cannot be laid on careful sampling and mixing the sample, for upon this the accuracy very largely rests.

**Estimating the Fat.**—It will be found more economical in some cases if 4 or multiples of 4 estimations are made at once. In this case the 2 double sockets will balance when placed opposite in the centrifuge. If but 1 or 2 estimations are made it will be necessary to balance the centrifuge by putting weights in the opposite socket. The weight of the clean, dry separating funnel must first be ascertained. This weight once found will suffice for all estimations made with that particular funnel.

I. *Weighing the Charge.*—Counterpoise the small beaker on the balance and carefully weigh out 20 gm. of the sample mixed as directed.

II. *Transferring the Charge to the Separating Funnel.*—Place the beaker containing the charge on a radiator or steam pipe until the butter is melted. (This may also be accomplished by adding a small quantity of boiling water.) Next pour the charge into the funnel, which must be maintained in an upright position, and no part of the charge lost in transferring. With a fine stream of hot water rinse down the sides of the beaker and pour the rinsings into the funnel. Repeat this, using not more than a teaspoonful of water at a time until the funnel is full to within  $\frac{1}{4}$  in. of the shoulder. The rinsing can be done very conveniently with the arrangement on many steam centrifuges for filling the Babcock test-bottles, *i.e.*, the rubber tube ending in a glass or metal point and connected with a water tank heated by steam. The point must be fine, however. Should it be larger than  $\frac{3}{16}$  in. it can be replaced with the tip of a small oil can. Should this arrangement not be at hand one can easily be improvised from a tin can, a rubber tube and an oil-can tip. In transferring the melted butter and rinsings the last drop may be prevented from running down the outside of the beaker by touching the lip of the beaker on the neck of the separating funnel.

III. *Centrifuging.*—Insert the separating funnel in the special socket, allowing the stem to project through the hole in the bottom and the handle of the stopcock through the open side. (Caution: The socket must always be placed in the centrifuge with the open side facing the direction in which the wheel revolves. This is very important, for if the opening faces the reverse direction the stopcock will be thrown out and broken.) Whirl 1 minute at the same speed used in testing milk on the Babcock method. The centrifuge must be kept warm.

IV. *Removing the Water.*—Remove the separating funnel from the socket and allow the water to flow through the stopcock until the fat (or curd) is within  $\frac{1}{8}$  in. of the stopcock. In this and subsequent operations care must be taken that the stopcock does not stick. It must always be under control, and it is best to give it frequent slight movements when the water or acid is running through it to be sure that this control is maintained,

otherwise it may stick at the critical moment and the estimation be lost. Most of the salt and part of the curd are taken out by the water. The remainder of the curd and all of the fat stay in the funnel.

**V. Dissolving the Curd.**—Measure out 9 c.c. of cold water (preferably distilled) into the beaker with the glass measure. Add to this 11 c.c. of sulphuric acid (sp. gr. 1.82–1.83) and mix by gently shaking. While still very hot add the mixture to the contents of the separating funnel. Now dissolve the curd by giving the funnel a circular motion with the hand grasping the neck. Centrifuge 1 minute, as before. Draw off the acid solution until the fat layer is within  $\frac{1}{4}$  in. from the stopcock and repeat the operations in this paragraph.

**VI. Freeing the Fat from the Acid Solution.**—The fat will now be in a clear transparent layer free from curd, and the solution below it will be practically colourless. To separate these, draw off the latter until the fat nearly reaches the stopcock, and centrifuge another minute. Allow the fat to descend through the stopcock until it just reaches the end of the capillary stem. This last step offers no difficulties, provided the stopcock is kept in control, but it requires care.

**VII. Estimating the Percentage of Fat.**—Carefully dry the separating funnel on the outside with a clean soft towel and weigh it. The weight thus obtained minus the weight of the empty funnel represents the weight of butter fat in 20 grm. of the sample. The percentage is obtained by dividing this weight by 2 and multiplying by 10.

Sometimes it is possible to obtain a clear layer of fat with but one addition of acid, but in the majority of cases it will be found necessary to add it a second time, as directed. The proportion of acid and water selected is the outcome of a number of experiments, and is the one which gives the best results. The test for fat alone involves 4 centrifugings of 1 minute each. The centrifuge should be kept warm and the contents of the funnel in a melted state when the acid is added. The time consumed should not be much longer than in testing cream by the Babcock test, and the operations involved are simple. No difficulty has been experienced in obtaining a clear fat. Occasionally a slight emulsion appears at the bottom of the fat layer when the latter is drawn into the stem. This is so small in amount that it does not seem to affect the accuracy of the test to any considerable extent. The emulsion should be weighed as fat and considered as such.

**Cleaning the Separating Funnels.**—The separating funnels should be washed after each estimation, but it is not necessary to dry them before use providing their weight, when clean and dry, has been found. The cleaning is easily done with hot water and either soap or cleansing powder. They should be well rinsed with clean water and drained.

### Estimation of Salt.

**Additional Apparatus Required.**—A 50 c.c. burette graduated to 0.1 c.c.

A 250 c.c. volumetric flask.

A 25 c.c. pipette.

A 250 c.c. beaker or white cup.

**Chemicals Required.**—An aqueous silver-nitrate solution containing 14.525 gm. pure silver nitrate per litre and a 10% aqueous solution of potassium chromate.

**Method.**—To determine the percentage of salt the wash water, obtained, as previously directed in Paragraph IV, is allowed to run into the 250 c.c. flask, and the operations in Paragraph IV conducted 3 times instead of but once, the water each time being allowed to run into the flask.

After the washings have become cool the flask is filled to the mark with cold water and the contents mixed. 25 c.c., which represent 2 gm. of the original sample, are then measured with the pipette into the beaker or cup and titrated with the silver-nitrate solution from the burette, using 2 or 3 drops of the potassium chromate solution as the indicator. The first appearance of a permanent red is the end point. The silver-nitrate solution is of such strength that 2 c.c. represent 1% of salt if a 1-gm. charge is used.

In the above test where 2 gm. are represented  $\left(\frac{25}{250} \times 20\right)$  the number of c.c. divided by 4 gives the percentage of salt in the original sample. As an example, if the burette reading showed that 10.6 c.c. of the silver-nitrate solution were consumed in reaching the end point, then 10.6 divided by 4, or 2.65, would be the percentage of salt in that particular sample.

### Estimating the Percentage of Curd.

If the moisture is determined in a separate charge by one of the reliable methods, the percentage of curd may be found by subtracting the sum of fat, salt, and moisture from 100.

**Benzoic Acid** (Compare Vol. II, p. 311).—Hinks<sup>1</sup> has devised the following method of detecting and estimating benzoic acid (and incidentally salicylic acid) in milk products.

10–20 gm. of cream are heated with an equal volume of concentrated hydrochloric acid until the curd is completely dissolved and the mixture is cooled and shaken with 25 c.c. of normal methylated ether and petroleum spirit (1 : 2). The ethereal layer is separated, and 1 drop of ammonia (0.880) added and then 5 c.c. of water. The mixture is shaken, the aqueous layer separated, heated for a few minutes on a water-bath to expel ammonia and then tested for benzoic acid, in the usual manner, with ferric chloride. It is probably advisable to add a trace of acetic acid before the ferric chloride,

<sup>1</sup> *Analyst*, 1914, 38, 555.

in order to ensure against alkalinity in the test solution, and in order to be certain that the ferric chloride solution is neutral, ammonia should be added to the freshly prepared solution till the iron precipitates, the solution filtered and the filtrate used for the test.

Hinks has shown that on adding ammonia to the ethereal extract (before the addition of water) a precipitate of ammonium benzoate appears, whilst in the case of pure milk, no effect, or only a slight opalescence is produced, and that the test is very delicate for benzoic acid. It is probable that it is in no way characteristic of benzoic acid but that other organic acids, probably lactic acid, would show a similar precipitate, for which reason, while note should be taken of this precipitate the result should be substantiated by the ferric chloride test.

The method is made quantitative by dissolving the cream as before, using a reflux condenser, the cooled solution being extracted 3 times with 20 c.c. of a mixture of equal parts of methylated and petroleum ethers. The mixed ethereal extracts are made alkaline with ammonia, 10 c.c. of water added and the mixture shaken, and the aqueous layer separated. This process is repeated twice more, adding more ammonia if necessary. The mixed aqueous extracts are made acid with hydrochloric acid and again extracted 3 times with 20 c.c. of mixed ethers. The combined ethereal extracts are allowed to evaporate spontaneously and the residue dried in a desiccator till constant in weight (about 24 hours). The residue is then heated at 100° for 1-2 hours and again weighed. The difference gives the benzoic acid in the original quantity of cream taken.

The method gives excellent results.

Butter should be shaken out violently with sufficient of a 1% solution of sodium bicarbonate, and the aqueous layer, after separation, boiled with hydrochloric acid and extracted with ether.

**Cinnamic Acid.**—This substance appears to be used occasionally as a preservative. In order to detect its presence the preservative is extracted, either as described under benzoic and salicylic acids (Vol. VIII, p. 190) up to the point of extracting the ether with barium hydroxide, or by Hinks' method (page 162). In either case the ether is extracted with ammonia, the aqueous layer evaporated to dryness, and the residue heated to boiling with 5 c.c. of dilute chromic acid solution (1 part dilute sulphuric acid (1:3) saturated with potassium dichromate and 7 parts water), in a covered crucible. The crucible is then cooled without opening and when cold the odour of benzaldehyde is at once noticed on removing the lid if so small a quantity as 0.2% of cinnamic acid is present in the original cream.

**Phytosteryl Acetate Test** (Compare Vol. II, p. 301).—The use of hardened vegetable fats has necessarily brought this test into greater prominence and utility, as it may be, in certain cases, the only method by which a hardened vegetable fat can be detected in admixture with animal fats.



The method of separating the sterols has been simplified by the use of digitonin which with these substances forms compounds almost insoluble in alcohol, and from which the original sterols are easily regenerated.

The method of applying the digitonin test first devised by Marcusson and Schilling<sup>1</sup> is given on page 118.

The method as thus devised gives difficulty sometimes as the digitonides form emulsions with the fat, and in any case it is only applicable if the sterols are present in the free state. It has been objected to by Klostermann<sup>2</sup> on the ground that esters of the sterols may be present and these are not precipitated by digitonin. He proposes to saponify the fat (100 grm.) with alcoholic potash in the ordinary way, and to dilute the saponified mass with water, acidify and extract the fatty acids and sterols with 250 c.c. of ether. The ether is washed with water and 250 c.c. of petroleum ether and 25 grm. sodium chloride are added. The water which separates is run off and the ether filtered through cotton wool. The filtrate is heated with 1 grm. of digitonin dissolved in 20 c.c. of 90% alcohol, and the crystalline precipitate which forms filtered after 15 minutes and washed free of oil with ether. This fat-free residue is then boiled with 20-30 c.c. of acetic anhydride, evaporated to dryness, dissolved in 50 c.c. of alcohol, and 25 c.c. of water gradually added. The precipitate is filtered off, washed with 70 c.c. alcohol, and recrystallised from 90% alcohol, in the usual way.

It is easier (particularly if more than 100 grm. of fat be used) to employ the method given by the writers (Vol. II) in which the fat is boiled out first with alcohol. The alcoholic extract is saponified once only, the fatty acids liberated, dissolved in ether, washed and treated direct with alcoholic digitonin solution (0.2 grm. digitonin per 100 grm. of fat). The digitonides are filtered and washed with ether to remove any traces of oil, dried and treated with acetic anhydride in the usual way, in an evaporating basin or stoppered tube (5 c.c. of acetic anhydride for 50 grm. of fat). The acetic anhydride is evaporated off and the residue taken up with absolute alcohol, and boiled if necessary with recently ignited animal charcoal (fine powder), filtered, evaporated to dryness and the residue recrystallised from 90% alcohol. The precipitation of the acetates from alcoholic solution by water, previous to final crystallisation as suggested by Klostermann (see *supra*) is not to be recommended, as the resultant liquid filters in some cases with great slowness. As it is generally necessary to crystallise the acetates 4 to 5 times, very small quantities of alcohol must be used for the recrystallisations and very small test-tubes should be employed. The crystals are filtered off in a very small funnel, having a glass bead fitting the neck. As each crop is thus filtered it is washed with 2 to 3 drops of 70% alcohol and the bead lifted and the crystals washed into a fresh tube with 1 to 2 c.c. of boiling 90% alcohol. The crystals are dissolved by heating and again allowed to separate. By thus avoiding

<sup>1</sup> Chem. Zeit., 1913, 37, 1001.

<sup>2</sup> Zeit. Unters. Nahr. Genussm., 1913, 26, 443.



filter paper, etc., no difficulty will be found in carrying even small quantities to 4 to 5 crystallisations.

A very small quantity of the crystals is placed on a porous tile and the melting point determined. Cholesteryl acetate melts at  $113^{\circ}$  C. (corr.), and phytosteryl acetate at from  $125^{\circ}$ – $133^{\circ}$  C. If the melting point of the fourth crystallisation be above  $116^{\circ}$  C. phytosterol may be assumed to be present in the original mixture.

**Rancidity** (Compare Vol. II, p. 313).—Recent investigations have added little to the knowledge of the causes of rancidity.

In the case of butter, it is necessary to distinguish two different types of rancidity which occur in practice. (1) The rapid change which takes place in butter after it has been placed on the market, particularly after it has been removed from cold storage, and is probably due entirely to the effect of light, possibly aided by the action of moulds. The change is confined to the outer layers of the butter. (2) The slow deterioration and loss of flavour which takes place when butter is kept in cold storage.

Investigation shows that sweet cream butter deteriorates much more rapidly than butter made from properly ripened cream; the lactic acid would appear to act as a preservative.

In spite of the fact that any lipolytic action on the fat appears to be negatived by the work of Rahn, Brown and Smith it is difficult to say that the deterioration in taste and rancid flavour may not be due to traces of free fatty acids such as cannot be actually estimated.

A most interesting investigation into the deterioration of storage butter has been made by Rogers and others<sup>1</sup> in which, amongst other possible factors, the action of small quantities of metals (particularly iron and copper) in producing deterioration has been investigated. As both these metals can easily be introduced into butter in minute quantities during making, and it is shown that they do produce decided deterioration, there appear to be grounds for attributing at least some of the loss of flavour to this cause. It is not improbable that the more rapid development of rancidity after removal from cold storage may be due to the preliminary stages having been so induced during storage.

The original bulletin should be consulted by those who are interested in the subject.

In connection with the general subject of faults in butter the following may be of interest and guidance to the analyst:

(1) A yeasty taste in butter may arise from repeated oversouring of the starter when yeasts develop which impart this flavour. Careless washing also intensifies this.<sup>2</sup>

(2) Lipolytic action may take place if starters are carelessly prepared,

<sup>1</sup> U. S. Dept. of Agric., Bureau of Animal Industry, Bulletin 162, April, 1913.

<sup>2</sup> Rosengren, *Milch Zentr.*, 1912, 41, 221.

or not used at all. Under these circumstances, according to Sohngen,<sup>1</sup> certain organisms may become sufficiently numerous to produce action on the fat, and in contradistinction to plant lipases, these microbic enzymes are distinctly thermostable. These organisms can be largely kept in a *bey-ance* by properly aërating the starter or cream and by the rapid development of acidity under proper conditions.

### Oleomargarine.

**Margarine** (Compare Vol. II, p. 313).—During the last few years the composition of margarine has undergone profound changes. These changes, which are still in progress, have rendered the analysis of modern margarine mixtures one of the most complicated problems with which the analyst can be confronted.

Except in the case of pastry and cooking margarines, the use of animal fats is rapidly ceasing. Their place has been taken by coconut and palm kernel products, which often reach 70% in the fatty mixture. As a certain percentage of butter fat is often present, which may either arise from the milk used in manufacture, or be purposely added to improve flavour, a recasting of the methods of analysis was imperative. A very large number of methods of dealing with these mixtures have been published, but the writers<sup>2</sup> are of the opinion that the original Reichert-Meissl method, with the additions of Polenske and Kirschner, is quite sufficient for the resolution of mixtures containing coconut and palm kernel products in the presence of butter fat and indifferent oils. It is only necessary to carry out the process in a standard manner, when the tables and curves proposed by the writers are applicable. *It must, however, be understood that unless the conditions of experiment are carefully adhered to, the tables, etc., will not apply.*

In order that any mistake may be avoided the method as used by the writers is here given.

5 grm. of the fat and 20 grm. of glycerol are weighed into a 300 c.c. flask, and 2 c.c. of 50% sodium hydroxide added. The flask is heated over a flame with constant shaking till it clears suddenly, the soap is then cooled and 100 c.c. of recently well-boiled distilled water are added, until the soap is dissolved. 0.1 grm. of powdered pumice, sieved through butter muslin, is added, and then 40 c.c. of sulphuric acid solution (20 to 25 c.c. of strong sulphuric acid diluted to 1,000 c.c., and the solution adjusted so that 35 c.c. neutralise 2 c.c. of the sodium hydroxide solution). The flask is at once connected with the condenser, and heated with a small flame till the insoluble acids are completely melted; the flame is then increased, and 110 c.c. distilled in 19 to 21 minutes. The temperature of the condenser water should be from 18° to 20° and the dimensions of the apparatus should be the same as given by Polenske

<sup>1</sup> *Abs. Cent. f. Bakt.*, Abt. II, 1912, 35, 331.

<sup>2</sup> *Analyst*, 1911, 36, 333 and with Richmond, *ibid*, 1912, 37, 183.

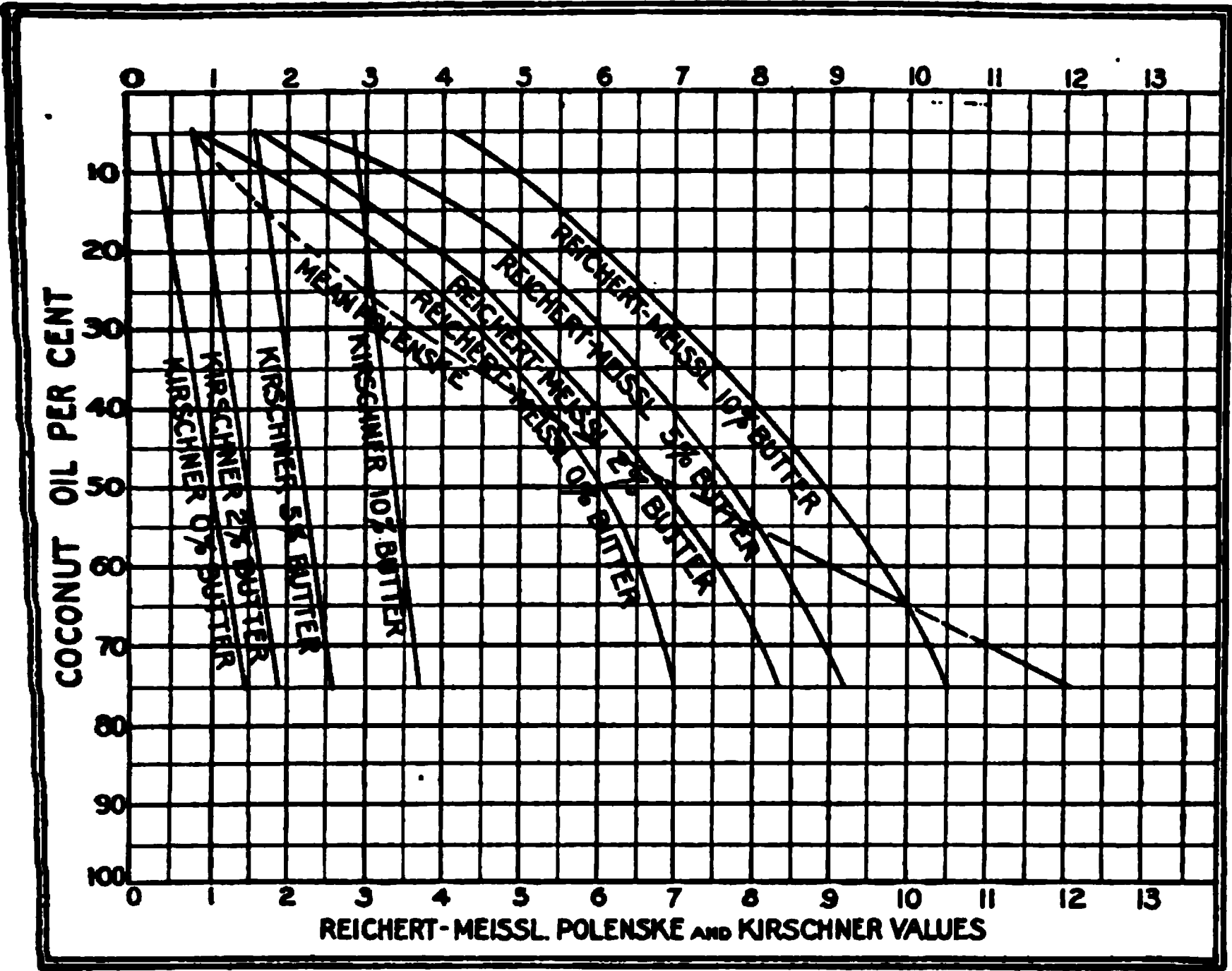


FIG. 8.

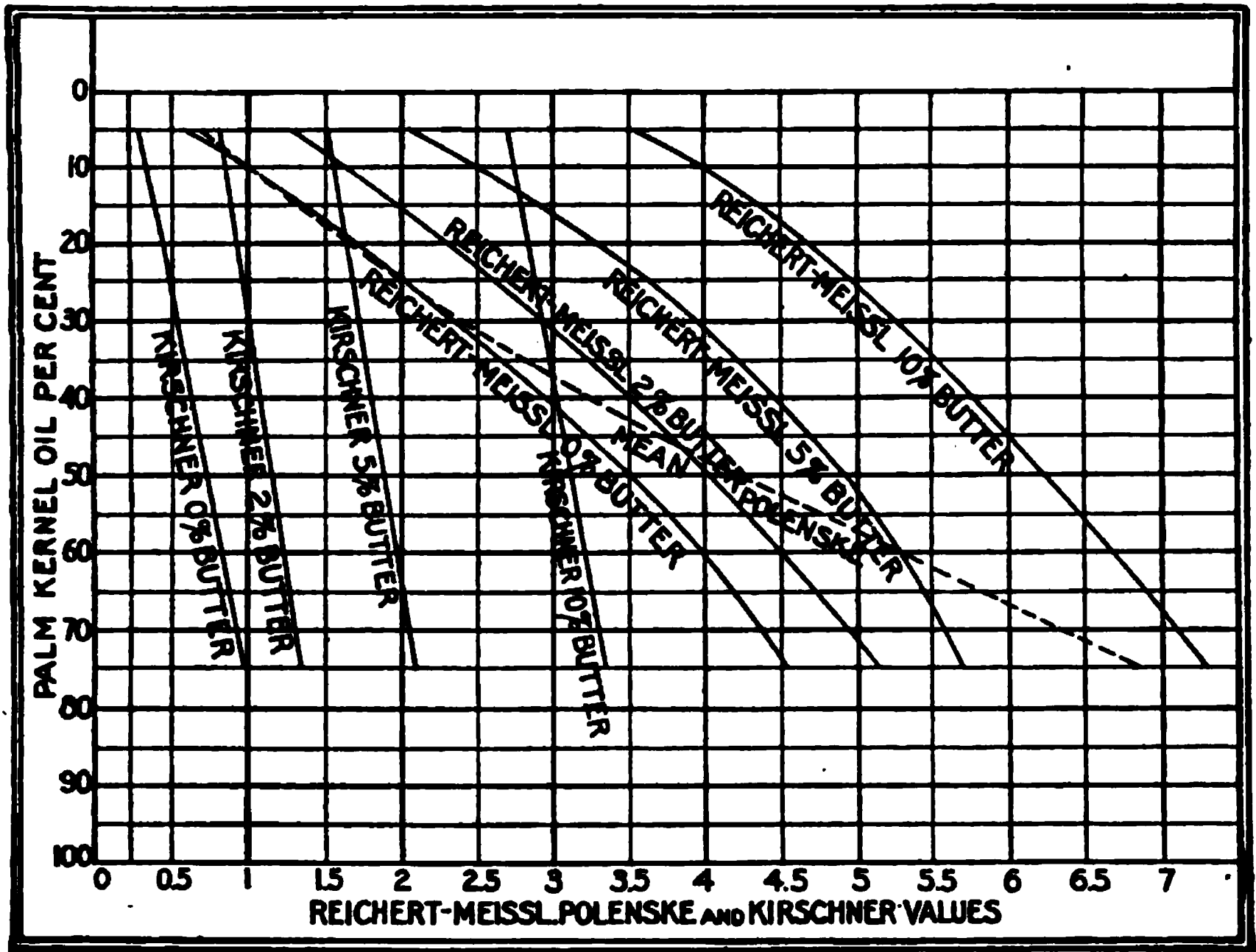


FIG. 9.

(see Vol. II, p. 295). When 110 c.c. have distilled, the flame is removed, and a 25 c.c. cylinder placed under the condenser to catch any drops. The 110 c.c. flask with its contents is immersed in water at 10° to 15° for 15 minutes. After mixing the contents of the 110 c.c. flask, they are filtered and 100 c.c. titrated with  $N/10$  baryta, using 0.5 c.c. of a 1% solution of phenolphthaleïn as indicator. This number of c.c. increased by  $\frac{1}{10}$ , after subtraction of the control (which must be determined in an exactly similar way, using all the reagents except the fat), is the Reichert-Meissl value. The condenser, cylinder, and 110 c.c. receiver, are washed with 18 c.c. of cold water, which are then poured over the filter used to filter the distillate, and rejected. The condenser is washed out with 4 successive portions of 10 c.c. of neutralised alcohol, which are received in the cylinder and poured over the filter into the 110 c.c. flask, the mixed alcohol solutions being then titrated with  $N/10$  baryta, using phenolphthaleïn as an indicator. A control value is obtained in a similar way. The number of c.c. of  $N/10$  baryta used, less the number used for the control, is the Polenske figure.

**Kirschner's Extension.**—To the 100 c.c. of the 110 c.c. distilled and titrated with baryta (care having been taken not to exceed the neutral point) is added 0.5 grm. of finely powdered silver sulphate, and the whole allowed to stand for an hour, with occasional shaking. The liquid is then filtered, 100 c.c. measured off, 35 c.c. of water and 10 c.c. of sulphuric acid (as previously employed) added, together with a long piece of aluminium wire, and 110 c.c. again distilled off in the standard Reichert-Polenske apparatus in 20 minutes; 100 c.c. are titrated, and the number of c.c. so obtained, corrected for the blank, is calculated to the Kirschner value by the following formula:

$$K = x \times \frac{121 \times (100 + y)}{10,000};$$

where  $x$  = the corrected Kirschner titration;

$y$  = the number of c.c. of baryta used to neutralise 100 c.c. of the Reichert-Meissl distillate.

From a number of experiments made by the writers the following general deductions were made:

(1) That for the Kirschner values for both coconut and palm kernel oils (with or without admixture of butter fat up to 10%), a straight line can be plotted which will represent, with very great closeness, the values experimentally obtained (see curves).

Further, for any percentage of coconut or palm kernel oils the difference in the Kirschner values for "no butter fat" and for any percentage of butter fat (up to 10%) will be proportional within very small limits to the percentage of butter fat; the closeness of the agreement indicates that the relation will also hold for higher percentages of butter fat.

(2) On examining the values obtained for coconut and palm kernel oils, it is seen that the Polenske value is practically independent of the amount of butter fat present, when present up to 10% in the mixture, and is practically dependent on the presence of the coconut or palm kernel oil only. The mean value was therefore calculated from the four values obtained for mixtures corresponding to each different percentage of coconut or palm kernel oil (see Table I), and on plotting these mean values a regular curve was obtained. The following equations have been worked out for these "mean value" curves:

$$\begin{aligned}x(\text{C.N.O.}) &= 12.3 (P - 0.45)^{0.747}; \\x(\text{P.K.O.}) &= 16.72 (P - 0.45)^{0.806};\end{aligned}$$

where  $x$  = the percentage of coconut or palm kernel oil.

(3) The Polenske value acts as an "indicator," so that when a margarine containing coconut or palm kernel oils is examined by the Reichert-Meissl-Polenske-Kirschner process, reference to the mean curve at once determines the percentage of coconut or palm kernel oil apart from other values. The corresponding Kirschner value obtained from the typical curve then determines the presence or absence of butter fat, the Reichert-Meissl value acting as a confirmatory figure, and controlling the small fluctuations which may in the Kirschner value be occasioned by a variation in butyric acid content of different butters.

On account of the similarity of the results obtained for coconut and palm kernel oils, the following formula will give the percentage of butter present with either fat for the Kirschner and Polenske values found experimentally:

$$\text{Butter per cent.} = \frac{K - (0.262P^{0.68} + 0.09)}{0.242};$$

or nearly as exactly by the more simple formula:

$$\text{Butter per cent.} = \frac{K - (0.1P + 0.24)}{0.244}.$$

The following formulæ connect the Kirschner value and percentage of butter fat when neither coconut nor palm kernel oil is present:

$K = 0.236B + 0.33$ , or, with a small increase in the probable error,  $K = 0.244B + 0.28$ , which is practically the formula given above.

The tables here given for coconut and palm kernel oils, with or without the admixture of butter fat, are the typical values obtained from the curves given above, and are a reliable guide provided the method be carried out under the standard conditions laid down, the standard apparatus being also employed (see Vol. II, p. 295).

It is necessary to draw attention to an observation which the writers have made recently. In the standard apparatus that part of the still-head which passes through the cork and into the interior of the distillation flask is pro-

vided with a small hole in the side to prevent the collection of condensed liquid in the still-head. As originally designed by Polenske, this hole had a fixed distance from the stopper of the flask. Insufficient attention is paid to this point by makers of the apparatus, and the writers have found that if the hole is much more than 1 cm. from the lower surface of the cork, low Polenske values may be obtained with high percentages of coconut oil; and that if this method be made a standard one, particular attention should be given to this point.

TABLE I.

Coconut oil, %	Polenske indicator value		Butter fat			
			0%	2%	5%	10%
0	0.45	Kirschner.....	0.18	0.80	1.49	2.70
		Reichert-Meissl.....	0.38	0.92	1.70	3.25
5	0.76	Kirschner.....	0.25	0.75	1.55	2.82
		Reichert-Meissl.....	0.87	1.65	2.15	4.10
10	1.22	Kirschner.....	0.34	0.84	1.60	2.90
		Reichert-Meissl.....	1.60	2.45	3.42	4.90
15	1.75	Kirschner.....	0.42	0.92	1.68	2.96
		Reichert-Meissl.....	2.52	3.15	4.35	5.55
25	2.91	Kirschner.....	0.60	1.08	1.82	3.08
		Reichert-Meissl.....	3.92	4.57	5.55	6.55
50	7.10	Kirschner.....	1.02	1.50	2.20	3.38
		Reichert-Meissl.....	6.05	6.88	7.72	8.95
75	12.19	Kirschner.....	1.45	1.92	2.55	3.70
		Reichert-Meissl.....	7.00	8.35	9.20	10.50
100	16.5	Kirschner.....	1.88	.....	.....	.....
		Reichert-Meissl.....	8.08	.....	.....	.....

TABLE II.

Palm-kernel oil, %	Polenske indicator value		Butter fat			
			0%	2%	5%	10%
0	0.45	Kirschner.....	0.18	0.80	1.49	2.70
		Reichert-Meissl.....	0.38	0.92	1.70	3.25
5	0.68	Kirschner.....	0.30	0.80	1.51	2.70
		Reichert-Meissl.....	0.53	1.27	2.05	3.50
10	1.00	Kirschner.....	0.35	0.85	1.54	2.75
		Reichert-Meissl.....	1.00	1.62	2.50	4.00
15	1.35	Kirschner.....	0.40	0.90	1.57	2.80
		Reichert-Meissl.....	1.35	2.00	2.90	4.35
25	1.97	Kirschner.....	0.48	0.97	1.65	2.87
		Reichert-Meissl.....	1.97	2.60	3.62	4.97
50	4.22	Kirschner.....	0.72	1.16	1.87	3.12
		Reichert-Meissl.....	3.50	4.05	4.92	6.22
75	6.87	Kirschner.....	0.97	1.35	2.07	3.35
		Reichert-Meissl.....	4.55	5.15	5.70	7.30
100	9.82	Kirschner.....	1.07	.....	.....	.....
		Reichert-Meissl.....	5.22	.....	.....	.....

These methods, while quite satisfactory so long as only coconut or palm-kernel oil is present, together with indifferent fats, leave a certain amount to the imagination if both coconut and palm-kernel oils are present together. The resolution of the mixture is then only possible when the percentage of the other fats or oils present is known, which is seldom the case, and it may not be possible to infer the quantity within 10 to 15%. Calculations based on the saponification values are often satisfactory, as by far the larger number of oils which are likely to be used with coconut and palm-kernel products have a saponification value in the neighbourhood of 192 to 195, and the figures for coconut and palm-kernel oils themselves are remarkably constant.

The following addition to the Polenske determination has been made by Burnett and Revis.<sup>1</sup> It gives information as to the relative percentages of coconut and palm-kernel oils in mixtures and may also on occasion throw light on the actual nature of the product present.

In an ordinary "straight" mixture of coconut and palm-kernel oils, the Polenske figure will determine the proportion with at least as great exactness as any other method. For instance, if the Polenske values are plotted as abscissæ, with percentage composition as ordinates, then a straight line joining the points which represent 100% coconut oil and 100% palm-kernel oil respectively will include the Polenske values for all mixtures of these two. The following process is for mixtures containing other constituents:

The ordinary Reichert-Meissl-Polenske determination is made in the *standard* apparatus and by the *standard* method. The Polenske figure is obtained using *N/10 baryta*. The insoluble barium salts are then filtered off on a hardened filter-paper under pressure and the salts washed 3 times with 3 c.c. of 93% alcohol (by vol.), the funnel being kept covered during filtration and washing. The paper after all possible alcohol has been sucked out, is dropped into a wide-mouthed CO<sub>2</sub> flask, 10 times the Polenske value in c.c.'s of 93% alcohol<sup>2</sup> (by vol.) added, and the flask boiled under a reflux condenser till the barium salts are in solution. About 5 c.c. of the hot solution are then poured rapidly into a strong test-tube (6 in. × ½ in.), which is at once closed with a stopper carrying a small bulb thermometer and aluminium wire stirrer. The liquid is rapidly stirred, holding the tube in a good light and the turbidity point noticed. The liquid is then warmed till again clear and the turbidity point again noted. This second temperature is taken as the turbidity temperature. If desired, the tube can be fixed in a wider tube so as to obtain slower cooling.

Working in this manner, coconut oil gives a turbidity temperature of 52.5° and palm-kernel oil of 68.5° and mixtures of these fats give temperatures between these limits proportionate to the percentage composition. The turbidity point is very sharp, is independent of the outside temperature and

<sup>1</sup> *Analyst*, 1913, 38, 255.

<sup>2</sup> The alcohol used in these experiments had a sp. gr. 0.8235 at  $\frac{15.5^\circ}{15.5^\circ}$ . Alcohol of the right strength may be obtained by placing 7 c.c. of water in a 100 c.c. flask and making up to the mark at 15.5° with Kahlbaum's absolute alcohol.



the barium salts, on which the test depends, are quite insoluble in the cold alcohol used for the Polenske determination. The turbidity points are also quite independent of the amounts of the 2 fats present in the original sample, but determine their relative percentages and so supply the necessary information. The strength of alcohol (93% by volume) must be strictly adhered to if the values here given are to be employed. It is the most satisfactory concentration. Other oils and fats (such as are likely to be present) do not interfere. In certain cases small quantities of insoluble volatile acids distil in the Polenske method, which give barium salts insoluble in boiling 93% alcohol. In such cases a clear solution cannot be obtained. The turbid liquid is therefore poured into a long test-tube, corked and kept upright in a water-bath at 70° to 71° until the solid matter has settled. The clear supernatant liquid is then poured off into the turbidity tube and the temperature of turbidity determined. This process does not affect the results. This *permanent* turbidity, due to barium salts of acids other than those derived from coconut and palm-kernel oils, must be distinguished carefully from that due to palm-kernel "stearine." The barium salts of the insoluble volatile acids of this "stearine" do not dissolve in 10 times the Polenske value in c.c. of 93% alcohol, but the liquid becomes more turbid *immediately* the flask is removed from the water-bath.

So long as mixtures of coconut oil and palm-kernel oil are dealt with, the above method gives good confirmatory evidence of the relative percentages. It has been found that coconut oils of different Polenske values give practically identical turbidity temperatures. It is to be noted that the filtration of the barium salts and their subsequent solution must be carried out *within a few hours of the Polenske titration*, as otherwise the salts become partially insoluble and the results are inaccurate.

Mixtures of the "oleines" and "stearines" are sometimes employed in place of the whole oils, but probably rarely. In these cases, although the turbidity temperatures do not give accurate information, on account of the very variable composition of these products, at the same time they give most useful information as to their presence.

The following table gives the results obtained with some of these products.

Fat	Reichert-Meissl	Polenske	Turbidity temperature, C.
Coconut oil.....	7.5	16.5	52.5
Palm-kernel oil.....	5.2	9.6	68.5
Palm-kernel "oleine".....	7.2	12.1	59.5
Palm-kernel "stearine".....	.....	8.2	72.5
Coconut "oleine".....	.....	.....	53.0 (calc.)
Coconut "stearine".....	.....	.....	63.0 (calc.)
Coconut "oleine," 80 per cent.....	8.24	17.05	54.5
Palm-kernel "oleine," 20 per cent.....			
Coconut "stearine," 60 per cent.....	4.43	9.93	67.0
Palm-kernel "stearine," 40 per cent.....			

It is interesting to note that cohune oil, which is analytically identical with coconut oil, gives exactly the same turbidity figures

### Hardened Fats.

The resolution of margarine mixtures has, however, been still further complicated by the introduction of "hardened" or "semi-hardened" fats (compare page 122). The process of hydrogenation completely destroys the identity of the original fat or oil, except in the case of the saponification value, and if the process be carried to any great extent the liquid vegetable oils begin to assume the properties of the solid animal fats.

The detection of hardened fats thus has become practically dependent on the detection of traces of the catalyst which is commonly nickel. The most delicate test for nickel is the following due to Atack<sup>1</sup> who uses *d*-benzil-dioxime as the reagent, which has been found to be much more delicate than diacetyldioxime which had been previously employed. Further, the activity of the former reagent is more circumscribed than of the latter (compare page 124).

50–100 grm. of the carefully filtered fat are ignited in a platinum or silica basin, or else shaken out with a 5% solution of hydrochloric acid (sp. gr. 1.14 to 1.16) and the acid aqueous extract concentrated on a water-bath and gently ignited. The residue in either case is taken up with very dilute hydrochloric acid (and if a platinum basin has been used transferred to porcelain), a drop of nitric acid added and the solution evaporated till almost dry; a large excess of ammonia (sp. gr. 0.925) is added and then a 0.2% solution of the reagent in ammoniacal solution. A rose-red colour or precipitate indicates nickel.

The relative proportion of ammonia in the reagent used in the above test has been found by the writers to be of importance, but as the personal equation is a factor, it is best for the investigator to make a few tests with known amounts of nickel in order to determine the most delicate combination.

It may be pointed out that a large number of carefully prepared hardened fats have been washed free of nickel by means of hydrochloric acid; these are therefore not detectable by the above process.

It may also be remembered that the process of hardening, if carried to a certain point, results theoretically in the production of a large proportion of triglycerides containing at least 1 molecule of stearic acid. From the observation of hardened fats there is a likelihood that molecules of considerable complexity are actually formed, but as this point has not yet been sufficiently investigated it will be accepted for the moment that stearic acid is the final product.

The presence of this acid in the triglycerides leads to the result that the

<sup>1</sup> *Analyst*, 1913, 36, 316.

usual microscopical test for stearin, after crystallisation of the fat from ether, may give misleading indications. For instance, the same fat hardened in the same manner may give crystals of different appearance, when crystallised in an identical manner on two different occasions. The crystals as a rule approximate to those of beef fat, but, in general, the crystalline conglomerates tend to radiate in all directions from a common centre, whilst the true beef fat conglomerate has usually the well-known fan-like appearance, though in some instances the crystals of hardened fats are practically identical with those of true beef fat.

For these reasons no infallible rules for guidance can be laid down and it is absolutely necessary for the investigator to familiarise himself with the various appearances by the actual examination of many hardened fats, which will enable him to recognise these fats in many circumstances in a way which no verbal description can impart.

From careful observation of these fats the writers venture to suggest that glycerides of varying complexity arise during the process of hydrogenation and if samples be taken at varying periods these complex glycerides behave like eutectic compounds when tested for the melting point, and they have good evidence which suggests that the melting point of the fat and the degree of hydrogenation if plotted as a curve would not result in a straight line.

**Analysis of Margarine.**—The writers very tentatively venture to suggest the following considerations as a guide to those who have to analyse margarine mixtures.

The disappearance of coconut and palm-kernel oils from the margarine industry is, in view of their extreme utility, very doubtful, and it is to be assumed that they will constitute the major part of the fatty mixture. Nothing as yet has arisen to invalidate the Reichert-Meissl-Polenske-Kirschner process and its findings may be taken as reliable, the further extension of Burnett and Revis being employed in doubtful cases.

The percentage of coconut and palm-kernel products being obtained, it is easy by calculation to arrive at the saponification value, iodine value, etc., of the remaining base.

This remainder may be all a hardened or a partially hardened fat, or a mixture of hardened fat and some other liquid vegetable oil.

If the various tests of Baudouin, Halphen, etc., give negative results, there is at least a probability that the base is all of a hardened variety. The nickel test is then applied, but the absence of nickel will not disprove the presence of hardened fat, though a positive result is of indicative value.

The microscopical appearance of the crystals (if any) obtained from a 25% solution of the fat in methylated ether (more or less according to the rapidity with which the crystals separate) will also point to the presence or absence of hardened fat.

Beyond the above indications analytical methods at the present moment avail but little, and, in any case, the nature of the hardened fat if diagnosed is distinctly problematical.

It has been assumed in the above outline that animal fats are absent.

### Ghee.

Ghee, in the strict sense of the word, is the pure clarified milk-fat of the buffalo, sheep, cow or the goat, but as has been shown by the writers<sup>1</sup> it is nearly always adulterated.

In the table below their figures are given for some 16 samples of ghee obtained from different parts of India.

The preparation of ghee is carried out in the following manner: the milk is boiled, immediately after milking, for 1 to 3 hours in earthen pots and when cold is inoculated with some sour milk. When curdled the whole of the milk is churned with a split bamboo for about half an hour, hot water added and the churning continued until the butter "comes." The butter is then skimmed off and kept for a short time when it becomes somewhat rancid.

The butter so produced is heated in an earthen pot until practically all the water present has been boiled away. It is then allowed to clarify and the clear fat, which constitutes ghee, is run into jars while warm.

The fats and oils used as adulterants are very numerous and comprise the carcass fat of various animals together with coconut, ground-nut, cottonseed, poppy-seed, sesame, safflower and niger-seed oils. Of the vegetable fats the most popular adulterant is obtained from the seeds of *B. butyraceæ*, a fat which is very like shea-nut oil in appearance and consistency but fortunately yields very different analytical figures (*vide* page 147). On account of this frequent substitution the fat of *B. butyraceæ* has come in some text-books to be referred to as "ghee."

Kesava-Menon<sup>2</sup> publishes a Reichert-Meissl value of 18.24 for 1 sample of ghee made from buffalo milk. This figure must be regarded as most abnormal and differs entirely from figures of pure ghee published by various observers.

<sup>1</sup> *Analyst*, 1910, 35, 343; 1911, 36, 392.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1910, 29, 1428.

## ANALYSES OF GHEE.

Source.....	Rangoon 75°.	Rangoon 71°.	Rangoon 57°.	Rangoon 53°.	Rangoon <sup>1</sup> 40°.	?	Ambala	Ambala	Ceylon
Price per cwt.....									
.....	30.58	30.42	18.04	11.88	0.44	23.34	20.3	31.5	31.0
.....	1.02	2.45	1.33	0.60	0.47	1.43	2.6	1.66	1.32
.....	228.8	228.7	213.9	206.7	193.4	219.1	223.8	220.1	215.0
.....	30.63	30.75	40.85	45.65	55.73	36.25	30.02	20.60	47.00
at 40° C. (Zeiss)	41.4	41.4	44.6	46.3	49.3	42.9	42.3	41.5	45.4
.....	24.0	24.5	47.5	63.0	95.0	.....	32.25	23.5	38.25
.....	0.8632	0.8637	0.8612	0.8603	0.8577	0.8609	0.8624	0.8631	0.8645
.....	312.8	312.6	202.4	282.5	264.4	290.5	305.8	313.5	204.0
.....	251.7	253.3	257.4	263.3	262.3	282.5	254.0	228.7	255.0
.....	61.1	59.3	36.7	25.1	1.1	17.0	50.0	64.8	39.0
.....	-9.4	-6.0	+19.0	+32.3	+62.2	+65.5	+4.0	-16.1	+16.0
leic), %	3.68	2.60	1.80	1.44	0.59	.....	1.52	2.59	2.56
.....	24.5	28.0	.....	.....	34.0	31.0	.....	.....	.....
%	Pure	Pure	Adulterated	Adulterated	Milk fat entirely absent	Adulterated	Slightly adulterated	Pure	Adulterated

1 Marked "Mixed with grease."

2 Avé Lallemant's process, see Vol. II, p. 288.

Bombay City					
Source	B	C	D	E	P
Reichert-Meissl value.....	25.70	26.20	28.40	29.80	25.60
Polariscope value.....	0.90	1.50	1.60	1.40	1.90
.....	213.80	223.60	224.90	225.40	221.40
.....	37.28	29.24	28.11	29.55	31.83
at 40° C. (Zeiss scale).....	44.30	44.80	43.00	42.00	42.00
.....	43.50	43.50	36.00	33.50	50.00
.....	0.8627	0.8619	0.8656	0.8656	0.8618
Lallemant's.....	292.30	305.60	307.50	308.10	302.70
.....	256.80	256.80	252.40	251.50	256.40
.....	35.50	49.40	55.10	56.60	46.30
.....	+21.30	+6.80	-2.70	-5.10	+10.10
.....	2.23%	2.39%	1.83%	1.84%	0.93%
leic), %	45.00	43.00	43.00	41.00	43.70
Inferences.....	Highly adulterated	Adulterated	Pure	Pure	Adulterated

## ERRATA IN VOL. II.

Page 290, in column 5 of the first table the Zeiss butyro-refractometer numbers given are at  $45^{\circ}$ , not at  $40^{\circ}$ , as stated. At  $40^{\circ}$  the numbers should read:

44.7

44.2

44.2

44.0

43.7

43.3

42.8

42.8

42.6

42.4

42.1

The last figure in the last column of the end table which is given +6.6 should read +6.0

# LARD.

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By C. AINSWORTH MITCHELL.

## DETECTION OF BEEF AND MUTTON FATS IN LARD.

Bömer<sup>1</sup> has based a method upon the fact that the difference between the melting point of  $\alpha$ -palmitodistearin (the characteristic glyceride of lard) and of its separated fatty acids is  $5.2^{\circ}$ , whereas, in the case of  $\beta$ -palmitodistearin of beef and mutton fats the difference is only  $0.1^{\circ}$ .

50 grm. of the melted lard are dissolved in 50 c.c. of ether and the solution allowed to stand at about  $15^{\circ}$ . The crystals are pressed between filter paper, recrystallised from 50 c.c. of ether and again pressed. Should the melting point be less than  $61^{\circ}$  the crystallisation must be repeated until that melting point is reached. The fatty acids are separated from part of the crystals and the melting point of the glycerides and fatty acids simultaneously determined.

Lards with glycerides melting between  $61^{\circ}$  and  $65^{\circ}$  C. must be regarded as adulterated if the melting point of the glycerides added to twice the difference between the melting points of the glycerides and their fatty acids gives a result lower than  $71^{\circ}$  C.

In the case of glycerides melting between  $60^{\circ}$  and  $61^{\circ}$  the presence of beef or mutton fat or of "hardened" oils, *q.v.*, is certain when the difference between the melting point is less than  $5^{\circ}$  and with glycerides melting from  $65^{\circ}$  to  $68.5^{\circ}$  when the difference is less than  $3^{\circ}$ .

For the detection of hardened oils the method may be used in conjunction with the phytosteryl acetate test.

By means of this test Bömer claims to be able to detect 5% of beef fat in lard containing coconut, arachis or cottonseed oils. Abnormal results due to the presence of fats such as shea butter could be checked by the phytosteryl acetate test (*q.v.*).

Hydrogenated arachis and sesame oils gave glycerides of high melting point ( $70.6^{\circ}$  to  $71.5^{\circ}$ ), while the corresponding fatty acids melted at  $68.6$  and  $68.5^{\circ}$ ; hence these glycerides apparently consisted of tristearin.

Hydrogenated cottonseed oil, however, gave a mixture of glycerides melting at  $61.3^{\circ}$  and containing fatty acids melting at  $38^{\circ}$ .

The melting point differences ranged from  $0^{\circ}$  to  $0.8^{\circ}$  for hardened arachis and sesame oils and reached  $2.8^{\circ}$  in the case of the cottonseed oil.

<sup>1</sup> *Zeit. Untersuch. Nahr. und Genussm.*, 1913, 26, 559; 1914, 27, 153.



These hardened fats lowered the difference in the melting point of lard to a greater extent than beef fat, from which, however, they could be distinguished by the phytosteryl acetate test.

The least soluble glycerides of the fat of sucking pigs and of pigs fed abnormally upon coconut, maize, sesame and cottonseed-oil cakes differed from those of normal lard in containing a smaller proportion of  $\alpha$ -palmito-distearin and more stearo-dipalmitin; but such abnormal feeding did not interfere with the detection of beef fat by this method.

A modification of Bömer's method will detect the presence of a small proportion of lard in coconut oil.

Sprinkmeyer and Diedrichs<sup>1</sup> find that the method will usually detect 5% of beef or mutton fat in lard. In the case of lards rendered in the laboratory the difference between the melting point of the least soluble glycerides and their fatty acids ranged from  $4.4^{\circ}$  to  $7.4^{\circ}$ , while Bömer's value (melting point of glycerides plus twice the difference between the melting point) varied from 73.1 to 76.5.

With beef and mutton fats the difference was  $0.8^{\circ}$  to  $1.2^{\circ}$  and the Bömer figure 65.2 to 67.3. Lard containing 5 to 10% of either foreign fat always gave a value below 72 and frequently below 70.

Hydrogenated oils depressed the Bömer value of the lard to the same extent as beef or mutton fat.

<sup>1</sup> *Zell. Untersuch. Nahr. Genussm.*, 1914, 27, 571.

# LINSEED OIL.

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By C. A. KLEIN.

Since Vol. II was written, linseed oil has been the subject of extended investigation and during the period covered by the present supplement, over 100 investigations have been published. These investigations have for the most part been directed towards perfecting methods of analysis and obtaining sound data as to natural or artificial variation in the characteristics of the oil. The years 1910-1914 have afforded excellent opportunities for investigation, because linseed oil varied from its normal price to nearly 100% above that figure.

In the following supplement in order to facilitate reference the same order of headings is maintained as that adopted in the original section.

**Cultivation.**—According to Eyre<sup>1</sup> at the present time there is a growing desire on the part of English agriculturists to return to the cultivation of flax and hemp. Especially is this manifest in Yorkshire, Somerset, Kent, and the East Central Counties, where at one time the cultivation of hemp and line—flax grown for fibre—figured largely in agricultural practice. A general account of the manner of raising good flax crops, and of their subsequent treatment, has been published by Eyre<sup>2</sup> wherein the possibility of reviving the flax industry in England is considered in the light of a report presented to the Development Commissioners in 1912.

Davidson<sup>3</sup> describes the results of a trial growing of flax at Wye (Kent, England).

Bolley<sup>4</sup> has investigated the supposed impoverishment of land devoted to flax culture, which in the past has given rise to the theory that the plant has an exhausting effect on soil, necessitating a change of source of supply.

The experiments of Bolley, carried out at the North Dakota Experimental Station disprove the theory of impoverishment, and establish the fact that flax "wilt" or flax-sick soil is caused by a fungus "*fusarium lini*," and that the fungus is usually introduced with the seed; simple treatment of the seed with formaldehyde will prevent the trouble.

**Preparation of Oil from Seed.**—Ennis<sup>5</sup> describes in detail modern methods, particularly those adopted in the U. S. A.; this work should be consulted

<sup>1</sup> *Chemical World*, 1913, 2, 310.

<sup>2</sup> *Science Progress*, 1913, 28.

<sup>3</sup> *J. S. Eastern Agric. College*, Wye, 1912, 21, 44.

<sup>4</sup> *Farmers' Bulletin*, 274 of U. S. A. Dept. of Agriculture.

<sup>5</sup> *Linseed Oil and Other Seed Oils*, D. Van Nostrand & Co., New York, 1909.

for technical points. From the standpoint of analysis and control it is germane to point out here that, according to Ennis, 85–90% of the linseed oil produced in the U. S. A. is obtained by crushing. The new process or “percolator” oil has not a high reputation, whilst the linseed meal produced by this process has a low content of oil, as is indicated in the analysis:

Oil.....	1.5 %
Water.....	9.18 %
Ash.....	4.90 %
Fibre.....	9.04 %
Albuminoids.....	41.6 %
Carbohydrates.....	33.78 %

Thorpe<sup>1</sup> quotes the following analysis of linseed cake by Kellner:

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Expressed.....	11.0	8.6	8.6	31.7	8.7	6.5
Extracted.....	10.2	37.4	3.8	32.7	9.1	6.8

See Millian<sup>2</sup> for method of detecting carbon disulphide in oil.

**Examination of Seeds.**—Sheppard<sup>3</sup> gives the following data obtained by the examination of linseed from different localities. The oil was obtained by pressing both the picked and original seed:

	Oil, %	Sp. gr., 15°	Av. weight per seed, mg.	Oleaginous impurities, %	Non-oleaginous impurities, %	Oil in total impurities, %
1. American.....	39.67	1.1413	4.61	1.5	1.69	10.1
2. American.....	39.40	.....	4.53	1.01	1.05	.....
3. La Plata.....	36.98	1.1415	5.56	0.58	5.64	14.1
4. Calcutta.....	40.82	1.1326	5.41	4.85	5.03	14.9
5. Bombay.....	41.23	1.1182	7.88	0.81	2.80	.....
6. S. Russia (Keitch).....	39.11	1.1375	5.74	5.05	1.71	.....
7. N. Russia.....	36.95	1.1458	4.19	3.31	1.97	.....

The oil content was determined by extraction. The average of 11 more recent samples of Calcutta seed was 6.90% of impurities, containing 15.1% oil. The average oil content of the cleaned seed was 41.01%.

Sheppard has made analyses of the oils expressed from the seed when new and after 2 years, and from his results concludes:

(1) Oil pressed from clean linseed does not differ materially from commercially pure linseed oil.

(2) The dark colour of La Plata oil is due to non-oleaginous impurities.

(3) A high percentage of oleaginous impurities does not affect the colour appreciably, but does affect the iodine value slightly.

(4) The technical manufacture of oil by the extraction process does not lower the iodine value.

(5) The constants of the oil pressed from the seed which had been kept 2½ years in a closed container do not appear to be affected by the ageing of the seed.

<sup>1</sup> *Dictionary of Applied Chem.*, Longman's, London, 1912, 3, 323.

<sup>2</sup> *Ann. Chem. Anal.*, 1912, 17, 1.

<sup>3</sup> *Journ. Ind. and Eng. Chem.*, 1912, 4, 14.

The following figures are of interest, representing oil extracted from linseed grown at Enfield Highway, Middlesex, England. The seed was sown in May, 1911, and the plants reaped in October. Owing to continued drought, the plants only attained an average height of 1 ft. and flowered very early. The seed was obviously low in oil content, as only 24.4% of oil could be obtained by extraction methods. The oil, extracted by ether from picked seeds was somewhat green in colour and had the following characteristics:

Sp. gr.....	0.931 at 15° C.
Acid No.....	3.3
Saponification No.....	191.9
Iodine No.....	177.4
M. P. of hexabromides from fatty acids.....	176.0° C.

Neville<sup>1</sup> states that the amount of mucilage in linseed is about 7%.

**Linseed Cake.**—In continuation of the work of Dunstan, Henry and Auld (Vol. II, p. 326) Auld<sup>2</sup> has found that the bulk of the samples examined yielded a proportion of the “available” hydrocyanic acid by simply moistening with water. The presence of unaltered enzyme thus demonstrated was ascribed to the increased adoption of oil presses of the Anderson type and the expression of the oil in the cold. The amount of hydrocyanic acid was in some cases only very small, and therefore negligible, but in others it was comparatively high and quite sufficient to be distinctly injurious. The amount found in the large number of linseed and mixed cakes examined during the present investigation varied from 0.001 to 0.056%, the latter amounting to 3.9 grains of HCN per pound, being produced by soaking the cake in water at a temperature of 38° C. for 6 hours. In this case, the material smelt strongly of hydrocyanic acid, and when fed to sheep either was not taken readily or made them very sick. The poisonous dose of such a cake is calculated to be one-third of a pound for a sheep and 2 pounds for a calf.

The methods of estimating the hydrocyanic acid are detailed in the original paper, the “total” hydrocyanic acid being obtained by distillation with 6% sulphuric acid and the “free” hydrocyanic acid by soaking in water at 38° C. and subsequently distilling.

The “total” hydrocyanic acid obtained in this way varied from 0.022 to 0.056%, and the free hydrocyanic acid from 0.009 to 0.052%.

Tables are given showing the velocity of formation at 38.5°; it is a function of the time, and is affected by feeding stuffs other than linseed cake. Brewers’ yeast appears to contain a cyanogenetic enzyme as it increases the production of hydrocyanic acid; green fodders without exception had an inhibiting effect, as also had glucose and molasses, but cane sugar was without action. Pure cellulose had an inhibiting effect, the cause being proved by experiment and on mathematical grounds to be due to the

<sup>1</sup> *Rep. Brit. Ass.*, 1911, 600.

<sup>2</sup> *J. S. E. Agric. College, Wye*, 1911, 20, 289.

formation of an adsorption compound of the cellulose and the enzyme, so that the latter was withdrawn from action.

Salts generally retard the action, as also do very weak acids (e.g., 1% HCl) and bicarbonate of soda, which were tried in connection with the effect of the digestive juices.

Experiments on animals proved that the cyanogenetic glucosides are not poisonous when taken in absence of the specific enzymes.

In conclusion the fact stated by Smetham may be emphasised, that if linseed meal is mixed with water much below boiling and then allowed to stand, there is great danger; in order to obviate this it is necessary when preparing a gruel to use boiling water, and to keep the mixture at a temperature of 80° C. or over for at least 40 minutes, under which conditions little or no hydrocyanic acid is likely to be liberated.

The rate of evolution of hydrocyanic acid under digestive conditions has been determined by Collins.<sup>1</sup> The amount of hydrocyanic acid yielded by linseed, and the rate at which it is formed, depend on the quantity of cyanogenetic glucosides, on the proportion of enzymes, on the temperature and on the degree of acidity. Normal digestive conditions were obtained as far as possible, and it is shown that, since the acidity of the stomach contents and also that of green grass is approximately  $N/20$ , linseed cannot under normal conditions produce hydrocyanic acid when fed to carnivorous or herbivorous animals, but abnormal conditions causing reduction of acidity would result in the liberation of hydrocyanic acid. For details the original paper should be consulted, or the undermentioned abstracts.<sup>2,3</sup>

Armstrong and Eyre<sup>4</sup> have applied the Guignard picrate paper test to the detection of hydrocyanic acid produced from the glucoside linamarin, and have found the method to be of extreme delicacy, as hydrocyanic acid can be so detected in a single flax seed. These investigators find that ripe seeds are free from cyanide, but that unripe seeds invariably contain it.

As the flax plant flowers over a considerable period, the harvested seed invariably contains a quantity of unripe seed, and to this cause the presence of linamarin in commercial linseed cake is attributed. The presence of cyanide in linseed cake is usually considered harmful, but the authors consider that instead of this being the case it might be that the peculiar value of linseed cake as a cattle food is determined to some extent by the liberation of small quantities of such a product. All species of *Linum* resembling ordinary flax in habit of growth, carrying white, blue or red flowers, contain more or less hydrocyanic acid, but in no case could this be detected in the yellow flowering species. The amount is subject to variation throughout the period of growth. The enzymic activity of *Linaceæ* is correlated with the presence of the gluco-

<sup>1</sup> *Proc. Durham Phil. Soc.*, 1912, 4, 99.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1912, 31, 507.

<sup>3</sup> *Analyst*, 1912, 37, 313.

<sup>4</sup> *Proc. Royal Soc.*, 1912, 85, B, 370.

side. The yellow flowering species have practically no action on glucosides and incidentally it must be recorded that these species are all slow in germinating and growth. The species containing cyanide are able to hydrolyse linamarin, prunasin and salicin: prunase accompanies linase in both *Phaseolus Lunatus* and in many *Linaceæ*, and as yet linase has not been found without prunase.

**Refining.**—No change of analytical importance can be recorded here.

**Technical Applications.**—The high prices which ruled during the early part of the period now covered, had an adverse influence on any new technical applications of the oil. Indeed many users were led to enquire into the technical properties of other drying oils with the result that in certain industries linseed oil has been replaced by the newer oils. This particularly applies to soja bean oil, menhaden oil, and china wood oil, which have replaced linseed oil to an appreciable extent—a change which has been rendered possible by the use of new drying agents. In this connection the papers of Gardner,<sup>1</sup> and Toch<sup>2</sup> should be consulted. China wood oil has been used most extensively as a substitute or rather as an improvement on linseed oil in varnishes. A varnish made from wood oil and rosin is stated to yield more satisfactory results than one prepared from the best Baltic linseed oil and hard gum resins. Mixtures of china wood oil with soja bean and menhaden oil have also been employed successfully in paints. Soja bean oil in white lead paint is considered by Zerr<sup>3</sup> to be preferable to linseed oil, which is of interest in view of the agreement of the German White Lead Cartell and Varnish Makers Assocn. that only linseed or poppy oil should be used.

**Chemical Composition.**—Haller<sup>4</sup> describes experiments on the “alcoholysis” of commercial samples of linseed oil. The oils investigated had iodine values ranging from 168–176, and saponification values from 185–191. Owing to the insolubility of linseed oil in methyl and ethyl alcohol, esterification was carried out, using benzene, carbon tetrachloride, acetone or ether as solvent. The mixture was boiled with alcohol containing 2.5% of hydrochloric acid. The esters so obtained were fractionated and identified. The methyl esters of palmitic, stearic, oleic, linoleic, linolenic, isolinolenic, and arachidic acid were obtained. Haller states that stearic acid was found in appreciable quantity, whilst the arachidic acid was present in only small quantity.

Erdmann and Bedford,<sup>5</sup> Erdmann, Bedford and Raspe<sup>6</sup> in continuation of previous studies, conclude that the linolenic acid of linseed oil exists in two stereoisomeric forms, which they designate  $\alpha$  and  $\beta$  respectively. The  $\alpha$  modification on bromination yields the insoluble hexabromide, whilst the  $\beta$

<sup>1</sup> *J. Frank Inst.*, 1911, 55.

<sup>2</sup> *Proc. Paint and Varnish Soc.*, London, 1910.

<sup>3</sup> *Oil and Col. Trades J.*, 1914, 46, 835.

<sup>4</sup> *Compt. rend.*, 1908, 146, 259.

<sup>5</sup> *Ber.*, 1909, 42, 1324.

<sup>6</sup> *Ber.*, 1909, 42, 1334.

variety yields the fluid tetrabromide. It is considered that the chemical composition of linolenic acid is expressed by the formula



Rollett<sup>1</sup> does not agree with these conclusions and considers that linolenic acid reduced from the hexabromides is an individual acid capable of yielding four distinct stereoisomeric addition bromides. For later discussion see Rollett<sup>2</sup> and Erdmann.<sup>3</sup>

Fahrion<sup>4</sup> gives the following percentage composition as representing normal linseed oil.

Unsataponifiable matter.....	0.6%
Saturated fatty acids.....	8.6%
Oleic acid.....	from 15.0-20.1%
Linoleic acid.....	30.0%
Linolenic acid.....	38.0%

By treating the fatty acids of linseed oil dissolved in chloroform with an excess of Hübl's iodine solution, and allowing the mixture to stand, Heiduschka and Rheinberger<sup>5</sup> have prepared trichlorotri-iodolinolenic acid,  $\text{C}_8\text{H}_{20}\text{O}_2(\text{ClI})_3$ , a white crystalline substance, m. p.  $95^\circ\text{C}$ ., soluble in chloroform and alcohol.

Morell<sup>6</sup> has examined the saturated acids of linseed oil. A yield of lead salts equal to 6% of saturated acids on the oil taken was obtained, and investigation of these salts showed that the composition of the mixed acids may be summarised as follows:

Stearic acid actually separated.....	51.7%
Stearic acid present in eutectic mixture.....	12.7
Palmitic acid present in eutectic mixture.....	20.0
Residual eutectic mixture.....	8.0
Oleic acid.....	4.0
	<hr/>
	96.4

It is observed that no daturic, myristic or arachidic acids were detected, but that the methods of separation of the saturated acids are very tedious, and new methods are wanted. By careful working, satisfactory results as to stearic acid are obtainable, but for palmitic, arachidic and myristic acids further investigation of their derivatives is necessary.

de Waele<sup>7</sup> elaborates and improves upon the Fachini-Dorta method of separating liquid from solid fatty acids in oils and fats as follows: 10 grm. of the dry fatty acids are dissolved in 90 c.c. of anhydrous acetone and 10 c.c. of  $N/1$  potassium hydroxide are added in a thin stream, constantly stirring. The vessel containing the mixture is then immersed in ice-water for 3-4 hours. The precipitated soaps of the solid acids are filtered off under suction and washed with acetone until the filtrate is colourless. The cake

<sup>1</sup> *Zeit. Physiol. Chem.*, 1909, 62, 422.

<sup>2</sup> *Zeit. Physiol. Chem.*, 1911, 70, 404.

<sup>3</sup> *Zeit. Physiol. Chem.*, 1911, 74, 179.

<sup>4</sup> *Zeit. angew. Chem.*, 1910, 23, 1106.

<sup>5</sup> *Chem. Zentr.*, 1911, 2, 772.

<sup>6</sup> *J. Soc. Chem. Ind.*, 1913, 32, 1091.

<sup>7</sup> *Analyst*, 1914, 39, 389.



of soap is then removed, dissolved in water with the aid of a little alkali, and the acids separated in the usual manner. The liquid acids in the filtrate can be separated by diluting with water, adding ether, and acidifying. The author claims that a higher iodine value for the liquid acids is obtained than that given by Tortelli and Ruggieri's method, and in addition the process gives quantitative results. The following figures are given for the amounts of saturated acids in various oils:

Linseed oil, Calcutta seed.....	9.1 % of iodine value 16.4
Linseed oil, Baltic seed.....	6.6 % of iodine value 20.0
Linseed oil, Northwestern.....	6.0 % of iodine value ....
Soja bean oil.....	13.8 % of iodine value 12.1
Para rubber seed oil.....	16.3 % of iodine value 10.7
China wood oil (varies considerably).....	54.1 % of iodine value ....
Crude menhaden oil.....	23.5 % of iodine value 20.2

**Preparation of Sample for Analysis.**—The Sub-Committee E of Committee D1 on Linseed Oil appointed by the American Society for Testing Materials (hereinafter referred to as A. S. T. M.) recommends:

"All tests to be made on oil which has been filtered at a temperature of between 60° and 80° F. through paper in the laboratory immediately before weighing out. The sample should be thoroughly agitated before the removal of a portion for filtration or analysis."

**Foots.**—Walker<sup>1</sup> determines foots by allowing a litre of oil to stand in a clear glass bottle for 8 days, and then noting the amount of sediment found. The highest grades of oil show no turbidity or "foots" by this test. The claim is made that sometimes the separation that could be called foots by the above method is caused by the freezing out of fats of rather high melting point. When a sufficient amount of the sample is available, heat one portion to 100° and set it aside for the determination of foots, together with a sample just as it is received. Note the odour of the warm oil, rubbing it on the hands; a small amount of fish oil may be detected this way.

**Break Test.**—Heat 50 c.c. of the oil in a beaker to 300° C. Note whether the oil remains unchanged, or "breaks;" that is, shows a jelly-like consistency.

Hertkorn<sup>2</sup> finds that flocculation of linseed oil in boiling is not only caused by carbohydrates or proteins from the seed, but frequently by adulteration with a fatty acid glyceride, which polymerises at 240–260° C. yielding insoluble gelatinous products. China wood oil and candle nut oil are the chief of these adulterants, but certain treated quick-drying train oils behave in the same manner in linseed oil when heated. In this case, however, only "thin" linseed oils could be so adulterated, owing to the greater viscosity of train oils as compared with that of normal linseed oil. It is pointed out that linseed oils containing only a few tenths of a per cent. of china wood oil gelatinise on heating to 240° C. so that adulteration which might not have been intentional would be detected by the test—the suggested unintentional adulteration being the storage of linseed oil in a

<sup>1</sup> *Bulletin* 109 (revised 1910), U. S. Dept. Agric. Bureau of Chemistry.

<sup>2</sup> *Chem. Zeit.*, 1910, 34, 462.

ask which had formerly held china wood oil. The value of Hertkorn's observation is debatable. de Waele states that linseed oil will sometimes show the presence of "Foots" by this test even after 9 months tanking.

**Specific Gravity.**—Bearse<sup>1</sup> has determined the density and thermal expansion of linseed oil with great precision. From this work it appears that if the density of any sample of pure linseed oil be determined at 25° its density at any other temperature between 10° and 40° may be calculated within the limits of ordinary experimental error by the use of the general equation

$$D_t = D_{25} + a(t - 25) + B(t - 25)^2$$

in which "*a*" is taken as  $-0.0006847$  and "*B*" as  $+0.000000120$ . Or the density may be measured at any other convenient temperature, and for short temperature intervals the corresponding value of "*a*" used.

The A. S. T. M. fix

	Max.	Min.
Sp. gr. at $\frac{15.5^\circ}{15.5}$ .....	0.936	0.932
or		
Sp. gr. at $\frac{25^\circ}{25}$ .....	0.931	0.927

for raw linseed oil from North American seed, and for the determination advise the use of an accurately standardised pycnometer, having a capacity of at least 25 c.c. A test is to be made at 15.5° C. water being taken as 1 at 15.5°, and another test at 25° C. water being taken as 1 at 25°.

Fahrion<sup>2</sup> considers that the above minimum figures are too high. In general, however, any figure below 0.931 demands further enquiry.

**Ash.**—Walker determines ash by burning 20 grm. of oil in a porcelain dish at as low a temperature as possible, and states that the best oil should contain only a trace of ash. An amount as large as 0.2% would indicate an adulterated or boiled oil. Ash should be examined for lead, manganese, and calcium.

Voorhees<sup>3</sup> found manganese in the ash of 16 samples of pure linseed oil, detecting this by the ammonium persulphate colouration test.

Boughton<sup>4</sup> has examined 16 samples of raw linseed oil of known purity and found them to contain ash varying in quantity from 0.02 to 0.21%. In every instance the ash contained manganese, the amount of which determined by the bismuthate method ranged from a faint trace to 0.0008% calculated on the original oil.

**Free Fatty Acids.**—The A. S. T. M. fixes 6.0 as maximum acid number, expressed in mgrm. of KOH per gram of oil. Walker determines the acid number as follows: weigh 10 grm. of oil in a 200 c.c. Erlenmeyer flask, add 50 c.c. of neutral alcohol, connect with a reflux condenser, and heat on a steam

<sup>1</sup> *Proc. Amer. Soc. Test Materials*, 1911, 11, 211.

<sup>2</sup> *Die Chemie der trocknenden Oele*, Springer, Berlin, 1911, 9.

<sup>3</sup> *Proc. Amer. Soc. Test. Matl.*, 1911, 11, 209.

<sup>4</sup> *U. S. Dept. Agric., Bureau of Chem.*, Circular No. 111, 1913 and *J. Ind. and Eng. Chem.*, 1913, 5, 281.

bath for half an hour. Remove from bath, cool, add phenolphthalein and titrate the free acid with  $N/5$  sodium hydroxide. The acid number varies with the age of the oil, and should be less than 8, though when the oil has been refined with sulphuric acid it may show a higher number: test for sulphuric acid.

**Unsaponifiable Matter.**—The A. S. T. M. fixes 1.5% as limit, and recommends the method of Boemer:<sup>1</sup> To 100 gm. of oil in a 1,000 to 1,500 c.c. Erlenmeyer flask add 60 c.c. of an aqueous solution of potassium hydroxide (200 gm. KOH dissolved in water and made up to 300 c.c.) and 140 c.c. of 95% alcohol. Connect with a reflux condenser and heat on the water-bath, shaking at first until the liquid becomes clear. Then heat for 1 hour with occasional shaking. Transfer while yet warm to a 2,000 c.c. separating funnel to which some water has been added, wash out the Erlenmeyer with water using in all 600 c.c. Cool, add 800 c.c. of ether and shake vigorously 1 minute. In a few minutes the ether solution separates perfectly clear. Draw off the soap and filter the ether (to remove last traces of soap) into a large Erlenmeyer flask and distill off the ether, adding if necessary 1 or 2 pieces of pumice stone. Shake the soap solution 3 times with 400 c.c. of ether, adding the extract to the first ether extract. To the residue left after distilling the ether add 3 c.c. of the solution of potash, and 7 c.c. of the 95% alcohol, and heat under reflux condenser for 10 minutes on the water-bath. Transfer to a small separating funnel, using 20 to 30 c.c. of water, and after cooling shake out with 2 portions of 100 c.c. of ether; wash the ether 3 times with 10 c.c. of water. After drawing off the last of the water, filter the ethereal solution so as to remove the last drops of water, distil off the ether, dry residue in a water oven and weigh.

**Iodine Value.**—The A. S. T. M. fixes 178 as the minimum Hanus value. Walker gives 174–193, and states that Gill has shown that a pure raw oil may give a value as low as 160. In the U. S. A. the Hanus method is largely used, whereas in England the Wijs method is more frequently adopted. In this connection Smith and Tuttle<sup>2</sup> have investigated the Hanus method, and found that concordant figures were obtained for raw linseed oil when the quantity of oil taken for a determination did not exceed 0.25 gm. When, however, a greater quantity of oil was used the iodine value was decreased. With burnt oils it was found that the limit of agreement diminished with an increased degree of burning. Variation of temperature was found to have more influence on the values obtained for burnt oils than was the case with raw or boiled oils.

Ingle<sup>3</sup> gives the following limits for samples of established purity:

Baltic oil.....	190–204 iodine value
Indian oils.....	180–189 iodine value
La Plata.....	175–186 iodine value
Black sea.....	176–182 iodine value
North American.....	177–188 iodine value
Morocco, Dutch and Turkish oils.....	185–192 iodine value

<sup>1</sup> Ubbelohde, *Handbuch der Öle u. Fette.*, 261–262.

<sup>2</sup> U. S. Bureau of Standards, Technologic paper No. 37; *J. Frank. Inst.*, 1914, 177, 687.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1911, 30, 344.

Ingle remarks that in all the foregoing values the exact method of determination is the important factor, and emphasizes the necessity of using pure reagents for this purpose. The method he used was that of Wijs.

It is difficult to fix absolute limits for the iodine value as is shown by the work of Meister<sup>1</sup> and Wolff<sup>2</sup> who have obtained low iodine values, viz., 157–166 from linseed oil of undoubted purity. Such figures are, however, not frequent, and would demand special inquiry. The writer considers that values below 165 should be regarded with some suspicion, and further investigation made.

Wilhelm and Meister<sup>3</sup> find glacial acetic acid is the best solvent for oxidised linseed oil (linoxyn or scrim oil), and advise its use in determining the iodine values of such products.

The extent of oxidation to which the oil has been submitted determines its solubility—highly oxidised oils being only partially soluble, even in hot acid. In spite of these drawbacks, the authors prefer this solvent in the place of chloroform or the solvents usually used. In the case of highly oxidised oils, the end point is not so distinct, as with the ordinary mixture.

de Waele finds that the use of a solvent is unnecessary in the examination of linoxyn, if the sample be comminuted by grinding in a mortar. An hour's soaking in chloroform or carbon tetrachloride previous to the addition of the Wijs (or other) solution will also serve to swell the substance and ensure its thorough interaction with the iodine reagent. Complete solution of oxidised oil or linoxyn is more satisfactorily obtained by the use of hot amyl alcohol or acetate as a solvent during 5–10 hours.

**Bromine Values.**—Vaubel<sup>4</sup> has devised a method of estimating the "Primary and Secondary Bromine Values of Oils." The results obtained are in close agreement with the iodine values of the oils, but the process does not appear to be of analytical importance at present.

**Insoluble Hexabromides.**—The test devised by Hehner and Mitchell<sup>5</sup> has received considerable attention, because of its great value in the analytical examination of linseed oil. Certain difficulties attend its use so that varying yields are frequently reported, and efforts have been and are being made to standardise the method of working.

**Qualitative.**—Eisenschmil and Copthorne<sup>6</sup> have devised a qualitative test for fish oils in vegetable oils, based on the insolubility of the fish oil bromides in chloroform, in distinction to the bromides of linseed oil, which are soluble. The method is described as follows: 100 drops of oil are dissolved in 6 c.c. of a mixture of equal volumes of chloroform and glacial acetic acid. Bromine is added drop by drop until the brown colouration remains. After 10 minutes the test-tubes are placed in a beaker containing boiling water.

<sup>1</sup> *Farb. Zeit.*, 1910, 16, 17.

<sup>2</sup> *Farb. Zeit.*, 1910, 16, 120.

<sup>3</sup> *Chem. Rev. Fett. Ind.*, 1910, 17, 260.

<sup>4</sup> *Zeits. angew. Chem.*, 1910, 23, 2077.

<sup>5</sup> *Analyst*, 1898, 23, 310.

<sup>6</sup> *J. Ind. and Eng. Chem.*, 1910, 2, 28.

Linseed oil and other vegetable oils will clear up completely within a few seconds, whilst fish oils will remain cloudy and give a sandy precipitate at the bottom of the tube within a short time. Fish oils that have been heated to 260° or more for some time will not respond to this test.

Trials made by the authors cited show that it is not possible to use this method for quantitative analysis unless a minimum of fish oil present is all that would be desired. The amount of insoluble bromides in oils of the same kind, but from different sources, varies to a considerable extent.

On account of heating and other oxidising processes to which the oils are subjected before they reach the market no reliable quantitative method will ever be worked out on the lines indicated above. The fact, however, that the precipitate formed can be weighed and is indeed in direct proportion to the amount of fish oil present in a given sample, raises this process above the level of an ordinary qualitative test; therein lies an advantage over other methods now in use. The short time required for the test and its applicability to both raw and boiled linseed oil are other factors of importance.

**Quantitative Methods.**—Ingle<sup>1</sup> applies the hexabromide test in the following manner: 1 to 1.5 gm. of oil are weighed out in tared beaker, and dissolved in 40 c.c. of ether (sp. gr. 0.720) to which 5 c.c. of glacial acetic acid have been added. Bromine is then run in until an excess is shown by the colour of the solution. The mixture is allowed to stand 6 hours, more bromine being added if necessary. After 6 hours the precipitate is collected on a tared filter paper, washed 4 times with 10 c.c. of ether, and after drying the flask (in which some of the precipitate often remains) together with the filter paper in the water-oven the weight of the hexabromide is obtained. Ingle obtained the following figures for samples of undoubted purity:

Oil	Iodine value	Sp. gr. at 15° C.	Hexabromides		M. p. ° C.
			1	2	
Baltic oil.....	197.0	0.9357	48.1	47.5	140-5
Calcutta oil.....	185.0	0.9322	39.1	39.3	140-4
Dutch crushed oil.....	182.5	0.9322	36.9	.....	140-5
English crushed oil.....	185.0	0.9332	40.0	.....	140-3
Plate oil.....	179.5	0.9315	35.3	33.7	140-5
Menhaden oil.....	182.0	0.9328	61.8	.....	decomposes
Tung oil.....	168.0	.....	nil	.....	.....

Ingle points out that the yields of hexabromides obtained by him are greater than those given by Hehner and Mitchell; experiments showed that variation in the time of contact with the bromine ether solution did not influence the yield.

Jensen<sup>2</sup> gives the following data in this connection; for method of preparation of hexabromides see original communication.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1911, 30, 344.

<sup>2</sup> *Pharm. J.*, 1911, 86, 839.

*Oil from laboratory-pressed River Plate seed:*

Ether insoluble hexabromoglyceride { 44.0 %  
118-141° m.p.

*Commercial sample, apparently genuine:*

Ether insoluble hexabromides from fatty acids { 44.9 %  
124-142° m.p.

*Adulterated sample (small quantity of fish oil):*

Ether insoluble hexabromides from fatty acids { 47.5 %  
125-143° m.p.

These figures are not in agreement with those usually obtained.

Sprinkmeyer and Diedrichs<sup>1</sup> using Hehner and Mitchell's original method, obtained 28.9% hexabromides.

Eibner and Muggenthaler<sup>2</sup> prepare the fatty acids with all precautions against oxidation, and then brominate at a temperature of  $-10^{\circ}$  C., subsequently filtering on asbestos. The original communication should be consulted for details of the method which, although lengthy, is probably the most exact yet recorded.

The authors made a large number of determinations on Raw linseed oil of different origin, and obtained yields of hexabromides as follows:

Dutch oils.....	51.73 %
La Plata oils.....	51.66 %
Indian oils.....	50.50 %
Baltic oils.....	57.96 %

The hexabromide value is not appreciably affected by the refining processes. The following values were obtained on applying the method to other oils:

Poppy oil.....	0.0 %
China wood oil.....	0.0 %
Perilla oil.....	64.12 %
Ocumi oil.....	60.98 %
Rape oil.....	6.34 %
Sofa bean oil.....	7.17 %

The authors show how rape oil can be quantitatively estimated in linseed oil. When the presence of rape oil has been proved by the erucic acid test, the approximate proportion of the adulterant can be calculated from the hexabromide value, 10% of rape oil reducing the hexabromide value of linseed oil by about 4.4%. 4% should be deducted from the value of rape oil found to allow for the permissible contamination of linseed oil by Cruciferæ.

Gemmell<sup>3</sup> prefers to brominate the fatty acids; for method and data, see page 119.

The percentage of bromine in the insoluble hexabromides varied from 67% to 68.5% against 70.96% for  $C_{17}H_{24}O_2Br_8$ .

Cod-liver oil yielded.....	35.20 %
Whale oil.....	21.70 %
Brown whale oil.....	25.8 %
Menhaden oil.....	51.7 %
Shark liver oil.....	17.70 %
Sperm oil.....	1.70 %

No definite relationship could be traced between the quantity of hexabromide and iodine value.

<sup>1</sup> *Zeit. Untersuch. Nahr. Genussm.*, 1912, 23, 679.

<sup>2</sup> *Forb. Zeit.*, 1912, 18, 131, et seq. or see abstract *Chem. Zentr.*, 1913, 1, 567; *Analyst*, 1913; *J. Soc. Chem. Ind.*, 1913, 32, 242; *Proc. Amer. Soc. Test. Mtrls.*, 1913, 13 393.

<sup>3</sup> *Analyst*, 1914, 39, 297.



For Sutcliffe's<sup>1</sup> method, see page 118.

At the present time no particular method can be definitely recommended, though for exact work the method of Eibner and Muggenthaler appears to be the best. In carrying out the test the writer finds that in order to obtain comparative results the following points must be recognised:

(1) For quantitative work some standardised method must be employed, and the yields compared with that given by a sample of known purity, determined under exactly the same conditions, and preferably at the same time.

(2) A low temperature is advisable.

(3) The hexabromides should be prepared from the fatty acids, otherwise, if fish oil be present, difficulty will be experienced in filtration.

(4) The melting point of the hexabromides should be determined. Hexabromides from linseed-oil glycerides melt at 143–147°; those from the fatty acids at 177°. 10% of fish oil can be readily detected, as the insoluble bromides obtained from such a mixture blacken and decompose instead of melting.

**Refractive Index.**—The A. S. T. M. advises using an Abbé Refractometer at 25° C. and fix 1.4805 and 1.4790 as maximum and minimum respectively.

Klimont<sup>2</sup> has determined the refraction constants of linseed oil according to the method of Procter,<sup>3</sup> and gives the following figures:

Refractive index.....	1.4705–1.4810
Mean molecular refraction.....	447
Saponification value.....	193.7

The mean molecular refraction was calculated from the formula

$$(n - 1) \frac{M}{d} \text{ or } \left( \frac{n^2 - 1}{n^2 + 2} \right) \frac{M}{d}$$

where  $n$  represents refractive index.

$d$  represents sp. gr. at same temperature.

$M$  represents mean molecular weight calculated from the saponification value.

White and Thomas<sup>4</sup> state that as the refractive index of china wood oil (1.5560 at 25° C.) is much higher than that of linseed oil, the determination of the refractive index might be of value in detecting adulteration. The increased viscosity of china wood oil at 50° may also be of use in this connection.

**Oxygen Absorption and Drying Test.**—The earlier method of Livache, Bishop and Weger, in which the increase in weight of films during drying was determined, has been modified by various workers.

Powney<sup>5</sup> from a series of experiments undertaken to determine the influence

<sup>1</sup> *Analyst*, 1914, 39, 28.

<sup>2</sup> *Zeit. angew. Chem.*, 1911, 24, 254.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1898, 24, 254.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1912, 4, 878.

<sup>5</sup> *Analyst*, 1910, 35, 192.



of turpentine and turpentine substitutes on the drying of linseed oil (boiled and raw) concludes:

(1) Except in the case of raw oil, none of the solvents accelerate the drying to any marked degree; turpentine is on the whole the most suitable.

(2) Suitable turpentine substitutes (such as the mixture of petroleum hydrocarbons and turpentine used in the experiments) may possess such relatively high efficiency as to warrant their employment for many purposes in place of pure turpentine.

A modification of the Livache method is due to Liverseege and Elsdon<sup>1</sup> in which 10 grm. of finely powdered litharge (dried to constancy at 20°–22°) is spread evenly over a flat bottomed dish of German silver 3 in. in diameter by 1 in. deep. The whole is weighed and 0.7 to 0.9 grm. of linseed oil added. After weighing, 5 c.c. methylated ether (0.720 sp. gr.) are added. The moistened litharge is spread evenly over the bottom by gently rocking the dish, which is then put into an incubator for one, two or more days until the weight is constant, or has passed its maximum. The gain in weight is expressed on the oil taken. The ether is almost wholly volatilised in 30 minutes, and tests show that the amount of non-volatile residue left therefrom does not exceed 3 mg., and is often less. The results of the test may be summed up as follows:

(1) Genuine raw linseed oil ceases to gain weight after 2 days, such gain being from about 15% to 18%, depending on the quality of the oil.

(2) Genuine boiled linseed oil ceases to gain after 1 day, the amount being fairly constant, viz., 12% to 14%.

(3) Whilst drying oils do not gain after about 2 days, non-drying oils may continue to do so for weeks.

(4) When oils of a particular class are compared, the gain in weight varies with the iodine value, and there is evidence of some relationship between the figures for oils of different classes.

Wilson and Heaven<sup>2</sup> have devised a method of determining the oxygen absorption of drying oils, which differs from those generally used, in that instead of determining the increase in weight of a drying film, they measure the volume of oxygen absorbed. The method has the merit of being rapid—1 hour's absorption at 100° being sufficient if the oil is distributed over a large surface.

The difference between the various classes of drying, semi-drying, and non-drying oils is clearly brought out by the results obtained. The method ignores, however, the evolution of volatile products during the drying of linseed oil, and thus far is open to criticism.

Krumbhaar<sup>3</sup> has modified the volumetric absorption method in such a way as to provide for the absorption of the volatile products. The oil is oxidised

<sup>1</sup> *J. Soc. Chem. Ind.*, 1912, 31, 207.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1912, 31, 565.

<sup>3</sup> *Chem. Rev.*, 1913, 20, 287.

in a large glass flask containing soda lime as absorbent of acid volatile products, and is connected with a paraffin oil eudiometer. Krumbhaar finds that  $9\frac{1}{2}$  hours at  $30^{\circ}$  C. suffices for the maximum absorption, and by calculation from the diminished pressure the volume of gas absorbed is obtained. An absorption of 41% was obtained, this being in agreement with the early result of Weger, viz., 43.7% (compare page 192).

Mannhardt<sup>1</sup> uses aluminum plates for the drying test. The apparatus consists of 5 such plates, 3 in.  $\times$  6 in., showing a total surface of 180 sq. in. The plates are held by an aluminum wire frame at intervals of about  $\frac{3}{8}$  in. The whole apparatus weighs less than 80 gm. and can be conveniently weighed on an analytical balance. The quantity of oil used is between 0.5 and 0.7 gm. It is usually applied at the rate of about 2 drops per surface, and is uniformly distributed with the tip of the finger. In order to obtain reliable results, observance of the following conditions is essential:

The tests should be carried out:

- (a) Along with a control oil of known purity or character.
- (b) Using uniform amounts of drier.
- (c) Using uniform temperature.
- (d) Using a definite limited thickness of film.
- (e) In an atmosphere of moderate humidity.
- (f) With free access of air.
- (g) Under the same degree of illumination.

Elsdon and Hawley<sup>2</sup> describe a method of detecting adulteration of linseed oil by a process involving oxidation for a specified time, followed by subsequent extraction and determination of unoxidised oil. The process is carried out as follows: 5 c.c. of a solution of 2.5 gm. of oil in 25 c.c. of ether are distributed over an Adam's coil of filter paper. After drying overnight, the coil is heated on the shelf of a steam-oven for 2 hours, and then extracted in a Soxhlet extractor for 3 hours, using ethyl ether (0.720) as solvent. The extract is evaporated and a little alcohol added to the residue, after which the extraction flask is heated for 2 hours in a steam oven, and then weighed. Ten samples of linseed oil gave 14.0% to 19.2% extract, colza oil 100.6%, linseed oil plus 20% colza oil, 21.0%; linseed oil plus 20% seal oil, 31.6%. It is suggested that the maximum permissible extract is represented by the equation

$$\text{Extract} = 81.9 - 0.35I$$

where  $I$  = iodine value (Wijs) and that routine testing should include the determination of iodine value and quantity of unoxidised extract as above.

In connection with this test it is to be noted that many cases of adulteration by semi-drying oils (excepting those at the bottom of the scale, e.g.,

<sup>1</sup> *J. Ind. Eng. Chem.*, 1913, 5, 129.

<sup>2</sup> *Analyst*, 1913, 38, 3.

cotton seed) would have to be in quantities well over 50% before any information would be learned from this method. An exception is to be made in the case of the so-called "drying" fish oils, menhaden, *e.g.*, which yield no ether-insoluble body whatever. This is the best test for a fish oil.

**Drying on Glass.**—Walker coats glass plates 3 in. × 4 in. with the oil to be examined, and exposes to air and light, noting when the film ceases to be tacky. A good oil should dry to an elastic film in 3 days. Varying conditions of light, temperature, and moisture have such an influence on drying tests that for comparison of one linseed oil with others all samples should be examined at the same time.

Davidson<sup>1</sup> has standardised a method of determining the rate of drying of oils on glass. In this method use is made of an incubator giving a constant temperature of 100° F. and a setting value is obtained by ascertaining the time required for a film of oil to become set as determined by its being sufficiently firm to bear the finger being drawn gently across it without leaving a whitish mark. Ten minutes is taken as the unit for the expression of the setting value. Concordant values appear to be obtained by the method which has been applied to a study of the action of driers on linseed oil.

**Qualitative Detection of Adulterants in Linseed Oil.**—To detect fish oils in linseed oil see "Hexabromide Test" by Eisenschmil and Copthorne (page 189).

Outerbridge, Jr.,<sup>2</sup> has shown that traces of mineral or rosin oil can be detected in linseed oil by the former showing a green and the latter a blue fluorescence when such a mixture is exposed to ultra-violet light (preferably an ordinary enclosed arc light) and examined against a black background. The author claims to have detected 0.1% of mineral oil in a mixture which by other methods appeared to be non-fluorescent. Samples of "debloomed" mineral oil (which by the light of an ordinary arc or in sunlight appeared free from bloom) became highly fluorescent when examined in ultra-violet rays. The test is not applicable to boiled or polymerised oils which in themselves are fluorescent.

Thurston<sup>3</sup> finds that the Liebermann-Storch test does not detect 50% of rosin oil in linseed oil, and that 1 drop of conc. nitric acid added to 5 drops of the oil gives a more reliable indication. Rosin or "gloss oil" gives a red-violet tint, changing to violet red. The same colour is given by 50% linseed-oil-rosin-oil mixture, whilst a yellow to greenish-yellow colour is given after standing a few seconds by mixtures containing 5%-25% of rosin oil.

Walker carries out the Liebermann-Storch test as follows: To 20 c.c. of oil add 50 c.c. alcohol, heat on steam-bath for 15 minutes, cool, decant the alcohol, evaporate to dryness, add 5 c.c. acetic anhydride, warm, cool, draw off the acetic anhydride and add a drop of sulphuric acid, 1.53 sp. gr. Rosin or rosin oil gives a fugitive violet colour.

<sup>1</sup> *Proc. Paint and Varnish Soc.*, London, 1908, 1910.

<sup>2</sup> *Proc. Amer. Soc. for Testing Matls.*, Philadelphia, 1911, 11, 1.

<sup>3</sup> *Oil, Paint and Drug Reporter*, 1914, 50.

The period of abnormally high prices previously referred to clearly showed that adulteration of linseed oil is not always easily detected. Clumsy adulteration with mineral oils or rosin is of course readily detected by analysis, but the experience of the writer is that such adulteration is rarely practised. The type of adulteration most difficult to detect is the admixture of linseed oil with other seed oils, the characteristics of which do not seriously affect those of linseed oil on admixture in reasonable proportion. The mixture can often only be classed as a low-grade oil and positive evidence was obtained of admixture of this description. The following example is one in which the mixing had been overdone, with the result that the oil, which had been tendered as "Genuine Linseed Oil," was refused, and damages established.

Unsaponifiable matter.....	1.39 %
Sp. gr. at 15½° C.....	0.9315
Acid number.....	6.72
Iodine value.....	148.5
Saponification value.....	175.7

The A. S. T. M. state that owing to the fact that it is possible to adulterate raw linseed oil with other vegetable oils to a considerable extent without detection, the sub-committee is working to devise a test of more value than those ordinarily in use. The determination of the hexabromides seems to offer possibilities, and in consequence the Society has decided to investigate this test.

**Interpretation of Abnormal Characteristics.**—The foregoing information refers principally to raw and refined linseed oil under normal conditions, and it now becomes necessary to point out in what manner the characteristics may be altered as a result of legitimate influences to which the oil has been submitted.

**Effect of Storage.**—Storage in closed vessels does not appear to effect any considerable change. The following values were obtained by the writer from a sample of genuine Baltic linseed oil, which had been stored in a closed vessel for 40 years:

Sp. gr. 15½° C.....	0.9348
Saponification value.....	190.3
Acid number.....	4.32
Iodine value.....	166.6
Unsaponifiable matter.....	0.67 %
Yield of hexabromides.....	22.4 %
M. p. of fatty acid, hexabromides.....	177.0° C.

These figures appear to confirm the opinion of Fahrion that during storage the unsaturated acids polymerise, but the effect is not very marked in a period of 40 years.

**Hydrolysis of Glycerides.**—Gardner<sup>1</sup> is of the opinion that certain changes which take place in oils and paints during storage are to be ascribed to auto-hydrolysis of the glycerides by enzymes or bacterial infection from low-class or imperfectly sterilised seed.

The most frequent effect observed is the increase in the free acid value

<sup>1</sup> *J. Franklin Inst.*, 1914, 5.

of the oil, and when certain pigments, particularly those having a lead base, are ground in such oil, there is a marked tendency to "livering," or the formation of granular lumps in the paint. To overcome the difficulty, it is desirable to heat cloudy linseed oil to 100° and so sterilise it; the cloudiness is considered to be an indication of possible contamination.

**Oil Extracted from Paints.**—Oil extracted from paints, although genuine, frequently yields abnormal values. The oil is often bleached by contact with the pigment.

Gardner<sup>1</sup> has determined the effect of pigments ground in linseed oil and finds that after 1 month's interaction with the oil, the pigment is readily detected in the case of lead and zinc compounds, as shown by the ash content of the extracted oil. Barytes, silica and other so-called inert pigments showed no change and the author is of opinion that the increased rate of drying observed by Sabin when using such mixtures must be ascribed to the increased surface presented and not to any chemically induced effect of the pigment.

More complete enquiries have been undertaken by Gardner,<sup>2</sup> and Boughton,<sup>3</sup> and the results of these workers are tabulated below.

## ORIGINAL OIL.

Pigment used	Sp. gr.			Ash, %			Iodine value			Acid value		
	G		B	G		B	G		B	G		B
	0.932		0.934	0.19		0.13	181.0		179.6	2.5		1.7
	2 years	1 year	2 years	2 years	1 year	2 years	2 years	1 year	2 years	2 years	1 year	2 years
White	Zinc oxide.....	0.9237	0.935	0.934	0.360	0.25	0.13	161.0	181.3	179.7	3.5	.....
	Basic carbonate white lead.	0.9372	0.940	0.938	1.149	0.35	0.40	157.5	175.0	177.3	8.6	.....
	"Leaded zinc".....	0.9389	.....	.....	0.922	.....	.....	157.4	.....	.....	5.7	.....
	Basic carbonate white lead 50 %...	.....	.....	.....	0.674	.....	.....	154.1	.....	.....	6.7	.....
	Zinc oxide 40 %.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	Barytes 10 %.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	Basic sulphate white lead 60 %.....	0.9334	.....	.....	0.626	.....	.....	157.8	.....	.....	5.6	.....
	Zinc oxide 40 %.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	Barytes.....	0.9325	.....	.....	0.212	.....	.....	169.6	.....	.....	3.5	.....
	Silica.....	0.9465	.....	.....	0.204	.....	.....	149.2	.....	.....	8.7	.....
Black	Kaolin containing CaSO <sub>4</sub> .....	.....	0.939	0.936	.....	0.12	0.14	.....	173.0	171.6	.....	.....
	Carbon black.....	0.9356	.....	.....	0.195	.....	.....	163.0	.....	.....	10.5	.....
	Graphite.....	.....	0.934	0.933	0.201	0.21	0.15	158.5	.....	.....	13.3	.....
	Artificial graphite.....	.....	0.935	0.939	.....	.....	0.15	.....	181.0	180.0	.....	.....
	Lamp black. (See carbon black).	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	Black magnetic oxide.....	.....	0.937	0.935	.....	0.17	0.13	.....	174.6	173.2	.....	.....
	Red lead.....	.....	.....	.....	15.56	.....	.....	135.4	.....	.....	19.2	.....
	Iron oxide.....	0.9457	0.941	0.939	0.456	0.15	0.14	156.3	173.8	172.5	8.6	.....
	Basic chromate of lead.	0.9390	.....	.....	1.271	.....	.....	156.7	.....	.....	8.3	.....
	Zinc chromate.....	.....	0.934	0.934	.....	0.20	0.18	.....	180.2	179.5	.....	.....
Yellow/Red	Chrome yellow.....	.....	0.937	0.935	.....	0.14	0.14	.....	176.3	175.7	.....	.....
	Chromium oxide.....	.....	0.937	0.937	.....	0.01	0.05	.....	178.0	180.2	.....	.....

<sup>1</sup> J. Ind. Eng. Chem., 1911, 3, 628.

<sup>2</sup> J. Franklin Inst., 1912, 174, 415.

<sup>3</sup> J. Ind. Eng. Chem., 1913.

The method adopted by Gardner consisted in grinding various pigments with linseed oil to paints of approximately the same consistency and leaving the products in air-tight vessels for nearly 2 years. The vessels were occasionally agitated for the first part of the period and finally were allowed to remain undisturbed for almost a year before examination. The vehicle was then extracted by benzene and petroleum ether and after removal of the solvent was examined, giving the results as summarised marked "G."

Boughton mixed the pigments with raw linseed oil and kept the mixtures in stoppered jars of uniform shape and size for periods of 1 and 2 years in dim diffused light. At the end of each period the contents of the jars were thoroughly mixed and samples taken. Ether was used for the extraction of the oil. The results are tabulated under "B," those obtained from the 1 and 2 year samples being so marked.

It will be seen that no general conclusions can be drawn from these figures. From a technical point of view the figures of Gardner more nearly represent actual conditions, although even here the information is not capable of general application. In practice the conditions differ considerably from those obtaining in the laboratory mixing of oil with pigments and the final results are not the same. The writer's experience shows that the changes taking place vary considerably, the variation being dependent on methods of manufacture. In practice the temperature of grinding is sometimes sufficient to cause to a small extent hydrolysis or polymerisation, depending on the presence of water or otherwise. The following figures show the variation which occurs:

	Ash, %	Sap. value	Sp. gr.	Iodine value
Oil from white-lead linseed-oil paste 10 years old.....	0.47	.....	.....	.....
Oil from white-lead linseed-oil paste 6 years old.....	0.03	.....	0.9534	116.0
Oil from white-lead linseed-oil paste 1 year old.....	.....	.....	0.9600	149.0
Oil from white-lead linseed-oil paste 3 months old.....	.....	.....	0.9500	142.5
Oil from white-lead soja-bean-oil paste 3 weeks old.....	.....	192.2	0.9410	112.3

In these circumstances no definite conclusion can be drawn and the possibility of interaction between oil and pigment must be recognised in the analysis of linseed oil extracted from paints.

**Drying of Linseed Oil.**—The problem of the drying of linseed oil has been further investigated by numerous workers, but little information of analytical importance obtained. The present position may be summarised as follows:

The drying of linseed oil is essentially an oxidation process, the final oxidation product being as yet unknown. During the drying process considerable quantities of volatile products are formed, the quantity depending on several factors. The so-called oxygen absorption figure obtained by ascertaining the increase in weight of a film of oil on exposure to air does not



represent the total quantity of oxygen actually taking part in the drying process, as no account is taken of that contained in the volatile products: thus Olsen and Ratner<sup>1</sup> found that after 74 days, drying linseed oil had increased in weight 18.05%, whilst the volatile products collected by potash and calcium chloride amounted to 5.21% and 14.55% respectively—the total oxygen absorbed (assuming the increase in weight of the KOH and CaCl<sub>2</sub> to be CO<sub>2</sub> and water) amounted to 37.80%, the linseed oil having lost 1.87% of its carbon and 14.73% of its hydrogen in the process of drying. Friend<sup>2</sup> after 65 days found an increase in weight of oil of 9.35%, whilst volatile products amounted to 14.94%, giving a total oxygen consumed of 24.29%. The variation in these figures illustrates the variable type of results obtained in investigations of this kind.

Sabin<sup>3</sup> has shown that films of linseed oil or paint containing linseed oil increase in weight to a maximum in less than a week, then these films begin to lose weight, though not so rapidly as they had gained.

With raw linseed oil the decrease in weight after 8 months was about 9/10 of the increase, and even at this stage the decrease was continuing. It therefore appears that the oxidation of linseed oil has no definite end-point, solid linoxyn apparently still losing volatile matters and becoming transformed into the fluid superoxidised linseed oil described by Reid. For analytical purposes the limitations of present experimental methods must be taken into account when considering the results obtained by the various methods proposed. The volatile products evolved during the drying of linseed oil have been shown to have definite germicidal value and the hygienic value of paint has been demonstrated in this connection. These products have been shown to contain the lower fatty acids and aldehydes. There is distinct evidence that the chemical constitution of the oxidised product and the volatile products evolved by drying oils varies with the temperature of oxidation.

Fahrion<sup>4</sup> from a study of the drying processes of linseed oil is of the opinion that the chemistry of the drying of the oil is essentially the same as that of the drying of the fatty acids and further that the addition of siccatives does not alter the process, except in so far as auto-oxidation is accelerated.

Fahrion<sup>5</sup> gives the following characteristics of a linoxyn film obtained by drying a film of linseed oil on glass plate for 10 days:

Fatty acids.....	25.3%
M. p. of acids.....	38.0° C.
Iodine value of acids.....	42.9
Hydroxy acids, soluble in ether.....	40.2%
Hydroxy acids, soluble in alcohol.....	20.2%
Iodine value.....	28.3
Hehner value.....	85.7

Ingle<sup>6</sup> is of the opinion that he has established the following points:

- <sup>1</sup> *Eighth Int. Cong. Appl. Chem.*, 1912, Sect. Ve Orig. Common., 12 165.
- <sup>2</sup> *Proc. Paint and Varnish Soc.*, London, 1914, 6, 145.
- <sup>3</sup> *J. Ind. Eng. Chem.*, 1911, 3, 2.
- <sup>4</sup> *Zeit. angew Chem.*, 1910, 23, 722.
- <sup>5</sup> *Farb. Zeit.*, 1912, 17, 2530 *et seq.*
- <sup>6</sup> *J. Soc. Chem. Ind.*, 1913, 32, 639.



(1) In the oxidation of a drying oil in air, the amount of oxygen absorbed in dry air is in the ratio of 2I to 2O, but if the air be moist the peroxides thus formed are decomposed with the production of volatile compounds—aldehydes and acids.

(2) That the free acids of linseed and other oils only absorb half the amount of that absorbed by their glycerides. The same remarks apply to their ethyl salts, these only absorbing 1 atom of oxygen for every 2 atoms of iodine absorbed.

Fritz and Zymandi<sup>1</sup> give the following values for oxidised linseed oil:

	Walton oil, 4 samples	Rapid oxidation oil, 2 samples	Runnings, 1 sample
Consistency.....	Hard.	Very soft.	Very soft.
Sp. gr. water at 4° C.....	1.0862 at 15° C. to 1.0734 at 21° C.	.....	1.0693 at 20° C.
Iodine value Wijs.....	61.8 to 65.5	96.2(1)	98.4
Ash.....	1.16% to 1.41%	0.15%(1)	4.36%
Unoxidised fatty acids.....	26.2% to 31.2%	43.5% to 49.4%	50.7%
Oxidised fatty acids.....	46.4% to 56.4%	42.1% to 42.5%	20.0%
Water soluble fatty acids.....	5.5% to 8.6%	2.7% to 5.7%	8.3%

**Driers.**—According to Metz<sup>2</sup> the German Lake and Colour Industry Protection Society have resolved that pure linseed varnish should not contain more than 2% of siccatives, or if resinates be employed, not more than 5%.

The more general adoption of cobalt driers and tung-oil driers is of sufficient importance to receive mention, as these driers are likely to be more frequently met with in the future.

**Influence of Light on Drying.**—Friend (*loc. cit.*) has investigated the influence of colour of pigments on the drying of paints, by using lakes of varying colours, the “base” of which was barium sulphate so selected because of its chemical inactivity.

**Boiled Oil.**—Ingle<sup>3</sup> shows the change in characteristics effected by the action of heat on linseed oil in the following table:

	Iodine value	Sp. gr.	Hexabromides
Original oil.....	179.5	0.9315	35.3
After 2 hours	175.5	0.9350	30.7
After 4 hours	170.0	0.9383	27.4
After 6 hours	165.0	0.9408	26.2
After 10 hours	154.0	0.9501	16.0
After 15½ hours	145.0	0.9583	10.5
After 43 hours	121.0	0.9800	0.9

The polymerisation effected by boiling is clearly shown in the above figures.

de Waele<sup>4</sup> gives a new and simplified method of estimating rosin in mixtures with oils, with a further application of the same method to determine

<sup>1</sup> Chem. Rev. Fett. Ind., 1914, 21, 43.  
<sup>2</sup> Chem. Zeit., 1911, 35, 473.  
<sup>3</sup> J. Soc. Chem. Ind., 1911, 30, 344.  
<sup>4</sup> Oil and Col. Trades' J., 1914, 46.

the glycerol in the oil. 10–20 gm. of the oil-rosin mixture are dissolved in at least twice its weight of amyl alcohol and about 1% of aqueous hydrochloric acid added. The mixture is kept on a steam bath under a reflux condenser for 2–3 hours after which esterification to amyl esters of the fatty acids will be complete, whilst the rosin acids will remain unesterified. The rosin is separated by neutralising with soda, separating off the aqueous layer and liberating the rosin acids under ether in the usual way, when they may be either weighed directly (using the factor of 1.07) or estimated volumetrically. The glycerol from the fatty oil may be separated and estimated by shaking out the original esterified mixture with water 2 or 3 times, when it will be found in an aqueous layer. It may be estimated by evaporating at 70° to a thick syrup and determining the concentration from the refractive index.

A private communication by the author giving details of tests of the methods was as follows:

#### COMPOSITION OF MIXTURES FOR TESTS.

Linseed oil (acid value 5.6).....	25.0 gm.
Pure oleic acid.....	12.5 gm.
Rosin.....	12.5 gm.
1. <i>Rosin determination:</i>	
Weight of mixture taken.....	5.6595 gm.
Weight of rosin obtained.....	1.3220 gm.
X 1.07.....	1.4145 gm.
Theory.....	1.4149 gm.
2. <i>Glycerol estimation:</i>	
Weight of mixture taken.....	20.4368 gm.
Weight of thick syrup.....	1.2262
Refractive index of same at 15.5° C.....	1.4571
Pure glycerol.....	1.084
Glycerol, %.....	5.3
Corresponding to fatty oil.....	50.5 %

**Blown Oils.**—Marcusson<sup>1</sup> has modified his earlier method<sup>2</sup> of distinguishing between blown rape oil and blown cottonseed oil in lubricating oils having a mineral oil base. In the improved method the fatty acids isolated as before are treated with light petroleum, and the soluble salts further examined by converting into the lead salts and determining the solubility of these in warm ether. The lead salts obtained from blown rape oil are almost completely soluble, whilst those from blown cottonseed oil are only partially soluble, the difference being exaggerated on cooling. By adopting this method, qualitative examination only is necessary, as 25% of blown cottonseed oil in blown rape oil can readily be detected.

The residue of insoluble lead salts calculated on the weight of soluble fatty acids taken from which they were prepared is 14–18% in the case of blown cottonseed oil, fish, and bone oils, and 8% in the case of a strongly oxidised linseed oil. This method is of value when combined with that of Sherman and Falk<sup>3</sup> in which the original iodine value of an oxidised oil is calculated from the increase in sp. gr. which takes place on blowing. For semi- or non-drying oils it is sufficient in practice to add 0.8 to the iodine

<sup>1</sup> *Mitt. K. K. Materialprüfungsamt.*, 1911, 29, 50.

<sup>2</sup> *Allen's Organic Analysis*, 1911., Vol. II, p. 370.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1906, 27, 605.

value of the oxidised oil for every increase of 0.001. in sp. gr. at 15/15° C. over that of the original oil. The iodine value of the oxidised oil can be taken as 90% of that of the oxidised acids and the sp. gr. of the original oil as 0.919 for rape and cottonseed oils. The normal iodine values of rape and cottonseed oil are fairly close, and therefore the qualitative test of Marcussen is of value in identifying the oil.

Fahrion<sup>1</sup> has further modified the method of estimating rosin in blown oils, in order to obtain increased accuracy. In this later method, 5 gm. of the oil (freed from metals) are dissolved in 50 c.c. petroleum ether and the solution treated with 20 c.c. of 96% alcohol, then neutralised with *N/1* alkali, using phenolphthalein as indicator. Water is then added to effect a dilution of about 60% alcohol and, after shaking, the mixture is allowed to stand over night. The soap solution is diluted to at least 200 c.c., acidified with hydrochloric acid and extracted twice with petroleum ether. The united extracts are esterified with absolute alcohol. After esterification is complete, phenolphthalein and *N/1* alkali are added until a red colour is just obtained. The solution is diluted with water until the alcohol is of 60% strength and from the alcoholic solution of the rosin soap the rosin acids are obtained in the usual way. Any traces of soap are removed from the solution of esters by washing with 10 c.c. of 60% alcohol and the washings added to the solution of the rosin soap.

It is pointed out that the fatty acids insoluble in petroleum spirit are more difficult to esterify in the case of oxidised oils than is the case with unoxidised oils. Thus, a known rosin-free blown oil gave a yield of 0.86 of apparent rosin by this method. Against this is the fact that colophony contains from 10 to 25% (average 14-15%) of neutral substances and hydroxyabietic acids, which escape determination. Fahrion uses the following corrections to compensate for errors created by the foregoing circumstances:

Amounts below 1% are ignored, those between 1 and 4% are taken directly as rosin, whilst figures above 4% are multiplied by 1.17, a factor corresponding to the average loss of 14-15% of neutral substances and hydroxyabietic acid.

According to de Waele (*loc. cit.*) the method already quoted can be used to estimate solid acids in an oxidised oil by working on the "fatty acids freed from oxidised acids" obtained in Fahrion's method of separation by petroleum ether. The author states that "polymerised acids" interfere with the process as these acids appear as "solid acids" but differ from them in that they have high iodine values and a different appearance.

See also Wolff and Scholze.<sup>2</sup>

For fuller information, on linseed oil, the work of Fahrion<sup>3</sup> is recommended.

<sup>1</sup> *Chem. Rev. Fett. Harz. Ind.*, 1913, 150 et seq.

<sup>2</sup> *Chem. Zeit.*, 1914, 38, 369.

<sup>3</sup> *Die Chemie der trocknenden Öle*, Springer, Berlin, 1911.

## ERRATA IN VOL. II.

Page 326, line 21, "Dunston" should read "Dunstan."

Page 329, line 19, "differs" should read "differ."

Page 331, line 12, delete the "p" after "increase."

Page 331, line 2 from bottom, "20.5-22.5" should read "205-225."

Page 342, bottom line, for "linolenic hexabromides" read "hexabromo-glycerides."

Page 343, line 1, after "decomposition" insert "at 143.5 to 144.5°, those prepared from the fatty acids."

Page 343 in table, under "Max.," for "0.836" read "0.936" and for "192" read "195."

Page 360, line 2 from bottom, for "Dunlap" read "Dunlop."

Page 365 line 4 from bottom for "Proctor" read "Procter."

# SOAPS.

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By J. R. POWELL.

In the following section no attempt is made to reorganise the methods of analysis given in Vol. II, but simply a few suggestions are given under the heads of the principal estimations, so as to include some other methods in general practice and some of the work that has recently appeared.

**Water.**—In estimating the volatile matter in soaps that are made from the drying or semi-drying oils, there is considerable danger of oxidation when the material is heated in the air-bath at a temperature of  $100^{\circ}$ . Even with soaps made from other stock, evidences of oxidation are easily detected if the heating is prolonged. Where this trouble is serious, the soap sample, prepared as suggested in Vol. II, should be dried to constant weight in a vacuum oven. R. M. Fitzpatrick<sup>1</sup> estimates the moisture by dissolving the soap in absolute alcohol, filtering, treating the filtrate with anhydrous sodium sulphate, refiltering, then evaporating the alcohol on the water-bath and finally drying in a steam oven. The moisture is calculated from the weight of alcohol insoluble matter and anhydrous soap found.

It is to be remembered that other substances besides water are volatile at a temperature of  $100^{\circ}$ , including alcohol, naphtha, benzene or other similar compounds that may have been added to the soap. Soap powders containing considerable quantities of sodium hydrogen carbonate, when heated, will suffer considerable loss of carbon dioxide which will have to be estimated and allowed for.

Alcohol, if present, may be estimated by distilling and determining the sp. gr. of the distillate (Vol. II, p. 424). When volatile solvents, immiscible with water, are present in considerable quantity, they may be estimated by distilling a quantity of the soap with steam, until oily drops no longer condense with the water. The distillate is collected in a flask with a narrow graduated neck, into which the oily distillate is finally floated and its volume read off and the weight calculated from the sp. gr. When foaming interferes, the soap may be precipitated by a heavy metal salt before distillation. Moisture may be estimated in such cases by distilling the soap with toluene or other suitable compound until no more water comes over and reading off the volume of water in the distillate.

<sup>1</sup> *Chem. News*, 1911, 104, 247.

**Separation of Substances Soluble in Petroleum Ether.**—The dried soap may be extracted directly with petroleum ether (Vol. II, p. 424), but since this extraction requires considerable time and care to insure its being complete, it is frequently more satisfactory to extract a solution of the soap (Vol. II, p. 430). However, as soap is very readily hydrolysed in water it is not permissible to use this solvent alone, as considerable quantities of fatty acids would be extracted besides the ether-soluble compounds existing free in the soap. It will be found that if a solvent consisting of about equal parts of water and alcohol be used, the hydrolysis of the soap will be so slight that no serious error will be introduced.<sup>1</sup> The solution obtained should be extracted by shaking out with several portions of petroleum ether. If troublesome emulsions are formed, they can usually be broken by the addition of a little more alcohol. Naturally this extraction gives both the unsaponified and unsaponifiable matter present. These may be separated by making an alcoholic potash or soda saponification of the residue obtained on the evaporation of petroleum ether, then extracting a second time, using the same precautions as above. This will give the unsaponifiable matter only (Vol. II, p. 426).

**Estimation of Fatty Acids.**—Instead of estimating the fatty acids by the cake method (Vol. II, p. 430) some analysts, after having decomposed the soap, prefer to dissolve the layer of acids in petroleum ether, drawing off the acid water by means of a separating funnel and filtering the ether solution into a tared flask or beaker. If the filter has previously been saturated with the petroleum ether and is kept saturated during the operation, any small quantities of the aqueous solution that may be accidentally transferred to the filter will be held back. After the solution has been extracted with several small portions of the petroleum ether and the funnel and filter carefully washed with the same, the solvent is evaporated and the acids weighed directly. A convenient method of driving off the last traces of petroleum ether is to heat the acids on a steam-bath under a moderate current of air directed into the flask or beaker from a suitable nozzle. It will be found that the acids may be brought to a more nearly constant weight by this method than by heating in an air-bath. The danger of oxidation of acids from the drying oils by this method should be noted and the use of a vacuum oven is recommended in such cases.

Whatever method is used in estimating the fatty acids, the danger of volatilisation must be considered. In fats having a saponification value of about 200, this danger is comparatively slight when reasonable care is used, but with fats containing acids of low molecular weight the loss may be very appreciable. Moreover in soaps that have become rancid with the development of a high free acidity, probably due to the decomposition of fat, volatile acids are present to a very considerable extent. Such a loss, if occurring,

<sup>1</sup> D. Holde, *Zeit. Elektrochem.*, 1910, 16, 436.

may be estimated by taking the fatty acids after weighing, dissolving them in neutral alcohol and titrating, then calculating the combined alkali from this titration. If the results so obtained are less than the combined alkali as estimated by other methods, the indication is that acids have been volatilised. This loss may also be checked by making two extractions, in one of which the acids are weighed and then titrated, whilst in the other the titration is made directly and a correction made in the weight for any loss indicated by a difference of titrations.<sup>1</sup>

It is almost impossible to separate or even extract the fatty acid from the decomposed mass obtained from soaps that contain large quantities of fillers insoluble in water or sodium silicate, which gives a gelatinous precipitate of silicic acid when decomposed with acid. When such difficulties arise, the best procedure is to separate the soap from such material by dissolving in alcohol, filtering and washing the matter insoluble in alcohol carefully so as to insure the removal of all soap. The alcohol is then evaporated and the fatty acids estimated in the purified soap obtained. Several methods have been proposed in which the soap is decomposed and the fatty acids collected in a narrow graduated tube, the volume read off and the weight calculated from the gravity. The method is rapid and with suitable apparatus quite accurate.<sup>2</sup> For a more detailed comparison and discussion of various methods of fatty acid estimation, see G. Fendler and L. Frank.<sup>3</sup>

**Examination of Fatty Acids.**—In the examination of fatty acids separated from a soap as described in Vol. II, p. 22, with the object of obtaining some idea as to their source, it is to be remembered that in the last few years fats from various sources hardened by hydrogenation have appeared on the market and are more or less extensively used in the manufacture of soap. Since the hardening of various oils converts the oleins and other unsaturated acids or their esters more or less completely into the corresponding saturated compounds, the characteristics of the fat are entirely changed. This is probably most noticed in the reduction in the iodine value and the rise in melting point or titer. Valuable information may, however, be obtained by the examination of the acids, as to the probable action of the soap in use and possibly as to the nature of fats required to make a similar product, but it would be very difficult to form even an approximate idea of the source of fats that have been used if they have been hydrogenated.

**Estimation of Free Alkali.**—When estimating the free caustic alkali by dissolving the soap in strong alcohol (Vol. II, p. 438), care should be taken to protect the solution from carbon dioxide or other acid fumes, as small quantities of alkali are easily neutralised in this way and so lost. The filter that is to be used should likewise first be neutralised by passing hot alcohol

<sup>1</sup> A. Besson, *Chem. Zeit.*, 1914, 38, 645 and 686.

<sup>2</sup> O. Schutte, *Seifensieder Ztg.*, 1913, 40, 551.

<sup>3</sup> *Zeit. angew. Chem.*, 1909, 22, 252 and 541.



of a slightly alkaline reaction through it until that coming through remains just alkaline.

Another method of estimating free alkali, sometimes used, is to make an aqueous solution of the soap, separate the soap by the addition of salt, filter off and wash the curd with saturated brine. To the filtrate barium chloride is added to precipitate the carbonates. The solution is again filtered and the free alkali hydroxide titrated in the filtrate. The precipitate of barium carbonate on the filter may be dissolved in standard acid, the excess titrated and the free carbonate calculated from the quantity of acid absorbed. If the free alkali hydroxide only is desired, both the soap and the carbonate may be precipitated directly from the aqueous solution with an excess of barium chloride and the hydroxide titrated in the filtrate.

Both methods may be refined if the most accurate work is desired. For a further comparison see E. Borshard and W. Huggenberg.<sup>1</sup>

**Matter Insoluble in Alcohol.**—This will, as stated in Vol. II, p. 438, be composed of the carbonate, silicate, borate and like alkaline salts of soda together with fillers insoluble in water. Frequently the only data required will be the weight of the insoluble portion in alcohol together with its total alkalinity. However, if a separate estimation of the various components is desired, it may be made as previously suggested (Vol. II, p. 441).

It is usually preferable to separate the water-soluble alkali from any insoluble filler that may be present and estimate the various alkalies in aliquots of the aqueous extract.

In this estimation, the variable composition of sodium silicate must be taken into consideration. This variation depends upon the composition of the original silicate and the amount of alkali used in the manufacture of the soap, as any excess of free caustic alkali used will tend to be absorbed by the silicate filler, causing the disappearance of free caustic and the formation of a more alkaline silicate. On this account, soaps containing an appreciable quantity of silicate filler usually show little or no free caustic alkalinity. Likewise since silicate of soda can be decomposed by carbon dioxide, soaps, especially in the chip form, that have contained large quantities of silicate of soda may have absorbed sufficient carbon dioxide during long exposure to the air to decompose the silicate more or less completely. In such cases, the quantity of carbonate will be increased and a corresponding quantity of free silicic acid found in the water insoluble portion. Since the combination of soda and silicic acid is so variable, it is preferable to determine the total alkalinity by titration, using methyl-orange and to determine the carbon dioxide, silicic acid and boric anhydride, if present, separately. After combining the proper quantity of soda with the carbon dioxide and boric acid found, the remaining sodium oxide and the silicon dioxide are reported as soda and silica combined as silicate, without attempting to use a definite formula for the silicate.

<sup>1</sup> *Zeit. angew. Chem.*, 1914, 27, 11.

Poetschke<sup>1</sup> has found that sodium borate is not entirely insoluble in alcohol and therefore recommends that the borax be estimated by fusing 10 gm. of the soap with 2 gm. of sodium carbonate and 0.15 gm. of fine silica. After disintegrating the fused product with boiling water, it is acidified with 20 c.c. of 1:1 hydrochloric acid, heated nearly to boiling and treated with slight excess of dry calcium carbonate. After boiling for 10 minutes under a reflux apparatus, the liquid is filtered and the filter washed, keeping the volume under 100 c.c. The filtrate is again boiled under the reflux, with the addition of a very small amount of calcium carbonate and cooled under partial vacuum by attaching a suction pump to the top of the reflux. Glycerin is then added to the cooled filtrate and the boric acid titrated. When an end point is obtained, more glycerin is added to see if it is permanent. 1 c.c. of *N*-solution is equivalent to 0.0505 gm. of anhydrous borax or 0.0955 gm. of borax crystallised with 10 molecules of water.

**Fillers Insoluble in Water.**—Although the soap may be dissolved directly in water and filtered (Vol. II, p. 429), the filtration of such a solution is usually very difficult and it is usually more convenient to separate the matter insoluble in water and alcohol together, as above, and weigh the portion insoluble in water after making the extract for the estimation of the alkaline carbonates, etc.

**Estimation of Special Constituents.**—Formaldehyde is present in a number of medicinal soap preparations and may be estimated as follows. The soap is dissolved in 4 or 5 times its weight of water and the soap precipitated either with barium chloride or sulphuric acid, filtered and made up to some definite volume. The formaldehyde is estimated in an aliquot of the filtrate by titrating by the iodometric method (Vol. I, p. 261).<sup>2</sup>

Peroxide soaps or powders are frequently met with in which the peroxy-gen component may be sodium perborate, percarbonate or the peroxide of some heavy metal, the nature of which will have been determined in the course of analysis. The available oxygen of such a soap may be estimated by dissolving the soap in water and decomposing with acid, care being taken that the solution is kept cool and sufficiently dilute to prevent the peroxide liberated from being decomposed. The acids are filtered off, using kieselguhr, if necessary, to obtain a clear filtrate, washing the residue and making up to volume. To an aliquot of the filtrate, potassium iodide is added and the liberated iodine titrated with standard sodium thiosulphate solution, or if preferred, the peroxide in the filtrate may be determined by acidifying with sulphuric acid and titrating with potassium permanganate,<sup>3</sup> 1 c.c. of an *N*/10 solution in either case being equivalent to 0.0008 gm. oxygen.

**Cresols.**—For a rapid assay of cresol soap preparations similar to the official disinfecting compounds, M. Seiger<sup>4</sup> proceeds as follows: 20 gm. of

<sup>1</sup> *J. Ind. Eng. Chem.*, 1913, 5, 645.

<sup>2</sup> O. Alleman, *Zeit. Anal. Chem.*, 1910, 49, 265; *Seifensieder Zig.*, 1913, 40, 49.

<sup>3</sup> F. M. Litterschied and P. B. Guggari, *Chem. Zeit.*, 1910, 37, 677 and 690.

<sup>4</sup> *Seifensieder Zig.*, 1911, 38, 986.

solution with the addition of 500 c.c. of water is twice evaporated to dryness to drive off the cresol. The residue is dissolved in 40 c.c. of water, transferred to a 160 c.c. graduated cylinder and decomposed by adding 5 gm. of sodium chloride and 10 c.c. of strong hydrochloric acid. 20 gm. of petroleum ether are added and the whole is shaken up and allowed to separate. 20 c.c. subtracted from the volume of the ether solution gives the volume of the fatty acid, which multiplied by 0.92 is considered the weight. Another 20 gm. of the original compound are diluted with 20 c.c. of water and treated exactly as above without previously evaporating. In this case, the upper layer consists of the cresols and fatty acid. The factor 1.04 is used to convert the volume of the cresols to the weight.

**Soap Powders, Scouring Powders and Scouring Soaps.**—The general methods of soap analysis will usually apply to products of the above class, but since the proportions of the various constituents are entirely different, precautions must sometimes be taken. In soap powders the percentage of soap is frequently quite low, the bulk of the powder being composed of sodium carbonate with water of crystallisation. In such cases, estimation of moisture, the weight of the alcohol extract, considered as true soap, and the alkalinity of the alcohol insoluble portion, calculated as sodium carbonate, may give all the data required. A qualitative examination of the matter insoluble in alcohol should be made, as various other alkalies may have been used, including sodium hydrogen carbonate, silicate, aluminate, triphosphate and borate. Potash salts are seldom found except in soft soaps both on account of their greater cost to the manufacturer and their hygroscopic nature.

Scouring powders usually consist of a large percentage of abrasive material with a comparatively small quantity of soap, moisture and alkali. Frequently a short method of assay, similar to that suggested above but including an estimation of water insoluble matter, would answer all requirements. A microscopic and more or less practical examination of the abrasive material might give valuable information. The abrasive material should be sharp and have decided mechanical cleansing value, but should not be too hard or it may be destructive to the surfaces on which it is used. Likewise, it should be practically free from extremely fine or clay-like impurities.

Scouring soaps are similar in their general composition to the powders described above, except they are in bar form. The quantity of abrasive material in such soap varies from an ordinary household bar soap containing a few per cent., to a scouring brick that contains only enough soap or other agent to act as a binding material.

The following table gives a list of typical analyses of various classes of soaps commonly found on the American market.

Kind of soap	Fatty anhydride	Rosin acids	Combined alkali	Free caustic	Free carbonate	Silicate <sup>1</sup> of soda	Salt	Water insoluble	Glycerin and undetermined	Volatile matter
Milled toilet.....	79.39	.....	9.24	0.08	0.37	.....	0.12	.....	0.38	10.42
Milled toilet.....	68.51	.....	7.98	0.12	0.55	.....	0.18	11.21 <sup>4</sup>	0.43	11.02
Floating.....	63.24	.....	8.23	0.02	0.33	.....	0.35	.....	0.52	27.31
Cocoa.....	57.95	.....	8.58	0.01	0.17	.....	0.21	.....	6.12	26.96
Transparent <sup>2</sup> .....	43.33	.....	5.50	0.12	0.73	.....	0.60	.....	10.51	24.58
Household bar, yellow..	41.56	18.83	6.30	0.04	1.87	2.38	0.28	trace	0.45	28.29
Household bar, yellow..	28.28	20.45	5.10	0.02	2.34	3.18	0.40	11.28 <sup>4</sup>	0.38	28.57
Household bar, white...	43.48	.....	5.64	0.02	2.05	11.11	0.23	.....	0.98	36.49
Laundry chip.....	78.99	.....	9.20	0.22	0.64	.....	0.10	.....	0.44	10.41
Laundry chip.....	57.54	.....	6.82	0.03	3.95	7.91	0.18	.....	0.70	22.87
Soft potash <sup>3</sup> .....	40.25	.....	6.92	0.06	1.19	.....	0.45	.....	5.92	45.21

## ERRATA IN VOL. II.

Page 373, in heading of 6th column of table B, "Insomeric" should read "Isomeric."

Page 381, line 12, for "212" read "213." Line 14, for "deducted" read "deduced."

Page 401, line 14 for "testing" read "heating."

<sup>1</sup> Silicate of soda calculated on the basis of 1 part of Na<sub>2</sub>O combining with 3.14 parts of SiO<sub>2</sub>.

<sup>2</sup> Contained 14.63% sugar.

<sup>3</sup> All alkalies calculated as potassium compounds.

<sup>4</sup> Water insoluble material was starch.

<sup>5</sup> Water insoluble material was silica.

# GLYCEROL.

By WILLIAM A. DAVIS.

**Specific Gravity.**—Redeterminations have been made by Kailan<sup>1</sup> of the sp. gr. of anhydrous glycerol at temperatures between 14 and 20°;  $d_{4}^{18^{\circ}} = 1.26414$  and  $d_{4}^{20^{\circ}} = 1.26082$ . The following equation gives the relation existing between sp. gr. and temperature:

$$d_{4}^{t^{\circ}} = 1.26413 + (15 + t)0.000632$$

A series of determinations of the boiling point of anhydrous glycerol under diminished pressure (32 to 9 mm.) was carried out, and values corroborating the vapour tensions given by Richardson<sup>2</sup> obtained. Experiments on the hygroscopicity of glycerin showed that in an atmosphere of average moisture content equilibrium is reached with a mixture containing about 80% of glycerol. Concentrated alcohol absorbs water about 4 times as rapidly as concentrated glycerol.

**Analysis of Crude Glycerol.**<sup>3</sup>—(International Standard Methods, 1911.)—The valuation of crude glycerol has in recent years assumed greater commercial importance owing to the increased value of the commodity. The want of uniformity in the methods and processes of analysis, together with the irregularity of the results obtained, emphasised the desirability for the standardisation of crude glycerol analysis; with this object in view, committees were formed in America, France, Germany and Great Britain. The methods detailed in this report have the unanimous support of each of the above committees, and are strongly recommended by them as International Standards.

**Sampling.**—The most satisfactory method available for sampling crude glycerol liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerol sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salts has taken place. In such cases he shall sample with a sectional sampler (a suitable sampling apparatus is described in an appendix to the report), then seal the drums, brand them with a number for identification and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler and a report

<sup>1</sup> *Zeit. anal. Chem.*, 1912, 51, 81.

<sup>2</sup> *Trans.*, 49, 764.

<sup>3</sup> *Analyst*, 1911, 36, 314.

of same made in his certificate, together with the temperature of the glycerol. Each drum must be sampled. Glycerol which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerol to be taken, including any deposit

**Analysis.**—(1) *Estimation of Free Alkali Hydroxide.*—Weigh 20 gm. of the sample into a 100 c.c. flask, dilute with approximately 50 c.c. of freshly boiled distilled water, add an excess of neutral barium chloride solution, 1 c.c. of phenolphthaleïn solution, make up to the mark and mix. Allow the precipitate to settle, draw off 50 c.c. of the clear liquid, and titrate with normal acid ( $N/1$ ). Calculate to percentage of  $\text{Na}_2\text{O}$  existing as alkali hydroxide.

(2) *Estimation of Ash and Total Alkalinity.*—Weigh 2 to 5 gm. of the sample in a platinum dish, burn off the glycerol over a luminous Argand burner or other source of heat giving a low flame temperature, the temperature being kept low to avoid volatilisation and the formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble organic matter, lixivate with hot distilled water, filter, wash and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate, and carefully ignite without fusion. Weigh the ash.

Dissolve the ash in distilled water and titrate total alkalinity, using as indicator, methyl-orange cold or litmus boiling.

(3) *Estimation of Alkali present as Carbonate.*—Take 10 gm. of the sample, dilute with 50 c.c. of distilled water, add sufficient  $N/1$  acid to neutralise the total alkali found at (2), boil under a reflux condenser for 15 to 20 minutes, wash down the condenser tube with distilled water free from carbon dioxide, and titrate back with  $N/1$  sodium hydroxide using phenolphthaleïn as indicator. Calculate the percentage of  $\text{Na}_2\text{O}$ . Deduct the  $\text{Na}_2\text{O}$  found in (1). The difference is the percentage of  $\text{Na}_2\text{O}$  existing as carbonate.

(4) *Alkali combined with Organic Acids.*—The sum of the percentages of  $\text{Na}_2\text{O}$  found at (1) and (3) deducted from the percentage found at (2) is a measure of the  $\text{Na}_2\text{O}$  or other alkali combined with organic acids.

(5) *Determination of Acidity.*—Take 10 gm. of the sample, dilute with 50 c.c. of distilled water free from carbon dioxide, and titrate with  $N/1$  sodium hydroxide and phenolphthaleïn. Express in terms of  $\text{Na}_2\text{O}$  required to neutralise 100 gm.

(6) *Estimation of Total Residue at 160° C.*—For this estimation the crude glycerol should be slightly alkaline with sodium carbonate, not exceeding the equivalent of 0.2 %  $\text{Na}_2\text{O}$ , in order to prevent loss of organic acids. To avoid formation of polyglycerols, this alkalinity must not be exceeded.

*Preparation of Glycerol.*—10 gm. of the sample are weighed into a 100 c.c. flask diluted with water and the calculated quantity of  $N/1$  hydrochloric acid



or sodium carbonate added to give the required degree of alkalinity. The flask is filled to 100 c.c., the contents mixed and 10 c.c. measured into a weighed Petri or similar dish 2.5 in. diameter and 0.5 in. deep, which should have a flat bottom. In the case of crude glycerols abnormally high in organic residue, a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30 to 40 mg.

*Evaporation of the Glycerol.*—The dish is placed on a water-bath (the top of the 160° C. oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven<sup>1</sup> measuring 12 in. cube, having an iron plate  $\frac{3}{4}$  in. thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf halfway up the oven. On these strips the dish containing the glycerol is placed.

If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130° to 140° C. can be readily maintained with the door partially open, and the glycerol, or most of it, should be evaporated off at this temperature. When only a slight vapour is seen to come off, the dish is removed and allowed to cool.

0.5 to 1 c.c. of water is added and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water-bath or top of the oven until the excess of water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spit. The time taken up to this point cannot be given definitely, nor is it important. Usually 2 to 3 hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° C. for 1 hour, when it is removed, cooled, the residue treated with water and the water evaporated as before. The residue is then subjected to a second baking of 1 hour, after which the dish is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, etc., is repeated until a constant loss of 1 to 1.5 mg. per hour is obtained.

*Corrections to be Applied to the Weight of the Total Residue.*—In the case of acid glycerol, a correction must be made for the alkali added. 1 c.c. *N*/1 alkali represents an addition of 0.022 gm. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the sodium hydroxide and carbonate to NaCl. The corrected weight, multiplied by 100, gives the percentage of *total residue at 160° C.*

<sup>1</sup> Grimwood (*J. Soc. Chem. Ind.*, 1913, 32, 1040) states that the type of oven specified here has proved quite unsatisfactory; a variation of 16° in the temperature was found on one shelf and between two shelves a maximum variation of 45° was experienced. Grimwood has described an electrically heated oven for the purpose of these estimations, which was designed so as to ensure uniformity of temperature throughout. An arrangement is provided to eliminate the glycerol vapour rapidly from the oven by means of an air blast, so as to facilitate the evaporation.

When a limited number of analyses have to be made it is probably best to use a Meyer vapour bath or an Abati oven (Vol. I, p. 69) heated by the vapour of a suitably chosen fraction of high boiling petroleum or turpentine; in this way the proper temperature can easily be ensured.



Preserve the total residue for the estimation of the non-volatile acetylisable impurities.

(7) *Organic Residue*.—Subtract the ash from the total residue at 160° C. Report as organic residue at 160° C. (*Note*.—It should be noted that alkaline salts of organic acids are converted to carbonates on ignition, and that the CO<sub>2</sub> radicle thus derived is not included in the organic residue.)

(8) *Moisture*.—This test is based on the fact that glycerol can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid or phosphoric anhydride.

2 to 3 gm. of very pure bulky asbestos, freed from acid soluble material, which has been previously dried in a water oven are placed in a small stoppered weighing bottle of about 15 c.c. capacity. The weighing bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid, under a pressure equivalent to 1 to 2 mm. of mercury, until constant in weight. From 1 to 1.5 gm. of the sample is then carefully dropped on the asbestos in such a way that it will be all absorbed. The weight is again taken, and the bottle replaced in the desiccator under 1 to 2 mm. pressure until constant in weight. At 15° C. the weight is constant in about 48 hours. At lower temperatures the test is prolonged.

The sulphuric acid in the desiccator must be frequently renewed.

**Acetin Process for Glycerol Estimation.**—This process is the one agreed upon at a Conference of Delegates from the American, British, French and German Committees, and has been confirmed by each of the above Committees as giving results nearer to the truth on crudes in general, and is the process to be used (if applicable) whenever only one method is employed. On pure glycerols the results are identical with those of the bichromate process. For the application of this process the crude glycerol should not contain over 50% of water.

The following reagents are required:

(1) *Best Acetic Anhydride*.—This should be carefully selected. A good sample must not require more than 0.1 c.c. normal sodium hydroxide for saponification of the impurities when a blank is run on 7.5 c.c. Only a slight colour should develop during digestion of the blank.

(2) *Pure Fused Sodium Acetate*.—The purchased salt is again completely fused in a platinum, silica, or nickel dish, avoiding charring, powdered quickly, and kept in a stoppered bottle or in a desiccator. It is most important that the sodium acetate be anhydrous.

(3) *A Solution of Sodium Hydroxide for Neutralising, of about N/1 Strength, Free from Carbonate*.—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide), and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

(4) *N/1 Sodium Hydroxide, Free from Carbonate*.—Prepared as above, and carefully standardised.

Some sodium hydroxide solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

(5) *N/1 Acid*.—Carefully standardised.

(6) *Phenolphthalein Solution*.—0.5% phenolphthalein in alcohol and neutralised.

**The Method.**—Into a narrow-mouthed flask (preferably round-bottomed) of capacity about 120 c.c., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25 to 1.5 gm. of the glycerol. Add first about 3 gm. of the anhydrous sodium acetate, then 7.5 c.c. of the acetic anhydride and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside.

The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used, it should have had a preliminary treatment with hot acetic anhydride vapour.

Heat the contents and keep just boiling for 1 hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat, and through the condenser tube add 50 c.c. of the carbon-dioxide-free distilled water, heated to about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapours from the flask on adding the water and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment. The contents of the flask may be warmed to, but must not exceed, 80° C. until solution is complete except a few dark flocks representing organic impurities in the crude. By giving the flask a rotatory motion, solution is more quickly effected. Cool the flask and contents without loosening from condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash the stopper or ground glass connection into the flask, and filter contents of flask through an acid-washed filter into a Jena glass flask of about 1 litre capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 c.c. of phenolphthalein solution (6), then run in sodium hydroxide solution (3) or (4) until a faint pinkish-yellow colour appears throughout the solution. This neutralisation must be done most carefully. The alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralised, as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon-

dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop, until the desired tint is obtained.

Now run in from a burette 50 c.c. or a calculated excess of  $N/1$  sodium hydroxide (4), and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser; cool as quickly as possible, and titrate excess of sodium hydroxide with  $N/1$  acid (5) until the pinkish-yellow or chosen end-point colour just remains. A further addition of the indicator at this point will cause a return of the pinkish colour; this must be neglected, and the first end point taken.

From the  $N/1$  sodium hydroxide consumed calculate the percentage of glycerol after making the correction for the blank test described below:

$$1 \text{ c.c. of } N/1 \text{ sodium hydroxide} = 0.03069 \text{ gm. of glycerol}$$

The coefficient of expansion for normal solutions is approximately 0.00033 per c.c. for each degree C. A correction should be made on this account if necessary.

**Blank Test.**—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride and sodium acetate as in the analysis. After neutralising the acetic acid, it is not necessary to add more than 5 c.c. of the  $N/1$  alkali (4), as that represents the excess of alkali usually left after saponification of the triacetin in the glycerol determination.

**Estimation of the Glycerol Value of the Acetylisable Impurities.**—The total residue at  $160^{\circ}$  C. is dissolved in 1 or 2 c.c. of water, washed into a clean acetylating flask, 120 c.c. capacity, and the water evaporated. Now add anhydrous sodium acetate and proceed as in the glycerol determination before described. Calculate the result to glycerol.

**Analysis of Acetic Anhydride.**—Into a weighed stoppered vessel, containing 10 to 20 c.c. of water, run about 2 c.c. of the anhydride, replace stopper and weigh; allow to stand, with occasional shaking, for several hours, till all anhydride is hydrolysed; then dilute to about 200 c.c., add phenolphthalein, and titrate with  $N/1$  sodium hydroxide. This gives the total acidity due to free acetic acid and acid formed from anhydride.

Into a stoppered weighing-bottle containing a known weight of recently distilled aniline (from 10 to 20 c.c.) measure about 2 c.c. of the sample, stopper, mix, allow to cool and weigh. Wash contents into about 200 c.c. of cold water and titrate acidity as before. This yields the acidity due to the original, preformed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated for 100 gm.) and double result, obtaining c.c. of  $N/1$  sodium hydroxide per 100 gm. sample. 1 c.c. of sodium hydroxide equals 0.0510 gm. of acetic anhydride.

**Dichromate Process for Glycerol Estimation.**—**MATERIALS REQUIRED.**—(a) *Pure potassium dichromate* powdered and dried in air free from dust or organic vapours, at  $110^{\circ}$  to  $120^{\circ}$  C. This is taken as the standard.

(b) *Dilute Dichromate Solution.*—7.4564 gm. of the above dichromate (a) are dissolved in distilled water and the solution made up to 1 litre at  $15.5^{\circ}$ .

(c) *Ferrous Ammonium Sulphate.*—Dissolve 3.7282 gm. of potassium dichromate (a) in 50 c.c. of water. Add 50 c.c. of 50% (by volume) sulphuric acid and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute dichromate (b). Calculate the value of the ferrous salt in terms of dichromate.

(d) *Silver Carbonate.*—This is prepared as required for each test from 140 c.c. of 0.5% silver sulphate solution by precipitation with about 4.9 c.c. *N/1* sodium carbonate solution (a little less than the calculated quantity of *N/1* sodium carbonate should be used; any excess of alkali carbonate prevents rapid settling). Settle, decant and wash once by decantation.

(e) *Subacetate of Lead.*—Boil a pure 10% lead acetate solution with an excess of litharge for 1 hour, keeping the volume constant and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(f) *Potassium Ferricyanide.*—A very dilute solution containing about 0.1%.

**The Method.**—Weigh 20 gm. of the glycerol, dilute to 250 c.c. and take 25 c.c. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes and add a slight excess (about 5 c.c. in most cases) of the basic lead acetate (e), allow to stand a few minutes, dilute with distilled water to 100 c.c. and then add 0.15 c.c. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 c.c., and return filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. (In the great majority of cases 5 c.c. is ample.) Occasionally a crude glycerol will be found requiring more and in this case another aliquot of 25 c.c. of the dilute glycerol should be taken and purified with 6 c.c. of the basic lead acetate. Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 c.c. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium dichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3.7282 gm. of the powdered potassium dichromate (a). Rinse down the dichromate with 25 c.c. of water and leave with occasional shaking until all the dichromate is dissolved (no reduction will take place).

Now add 50 c.c. of 50% sulphuric acid (by volume) and immerse the

vessel in boiling water for 2 hours and keep protected from dust and organic vapours, such as alcohol, until the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (*c*), making spot tests on a porcelain plate with the potassium ferricyanide (*f*). Titrate back with the dilute dichromate. From the amount of dichromate reduced calculate the percentage of glycerol.

1 grm. glycerol equals 7.4564 grm. dichromate.

1 grm. dichromate equals 0.13411 grm. glycerol.

**Notes.**—(1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(2) Before the dichromate is added to the glycerol solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process.

(3) For “crudes” practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0.5 c.c.

(4) It is sometimes advisable to add a little potassium sulphate to insure a clear filtrate.

**Instructions for Calculating Actual Glycerol Content.**—(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylisable impurities, if any be present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylisable impurities are present, these are included in this figure.

**Notes and Recommendations.**—Experience has shown that in crude glycerol of good commercial quality the sum of water, total residue at 160° C. and corrected acetin results comes to within 0.5 of 100. Further in such “crudes” the dichromate result agrees with the uncorrected acetin result to within 1%.

In the event of greater differences being found, impurities, such as polyglycerols or trimethyleneglycol, are present. Trimethyleneglycol is more volatile than glycerol; it can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the divergence between the acetin and dichromate results of such distillates, trimethylene-glycol showing by the former method 80.69%, and by the latter 138.3%, expressed as glycerol.

In valuing crude glycerol for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites and thiosulphates. The methods for detecting and determining these impurities have not formed the subject of this investigation.

**Recommendations by Executive Committee.**—If the non-volatile organic residue at 160° C. in the case of a soap lye “crude” be over 2.5%—*i.e.*, when

not corrected for carbon dioxide in the ash—then the residue shall be examined by the acetin method, and any excess of glycerol found over 0.5% shall be deducted from the acetin figure.

In the case of saponification, distillation and similar glycerol, the limit of organic residue which should be passed without further examination shall be fixed at 1%. In the event of the sample containing more than 1%, the organic residue must be acetylated and any glycerol found (after making the deduction of 0.5%) shall be deducted from the percentage of glycerol found by the acetin test.

**British Standard Specifications for Crude Glycerins.**—The following standard specifications were drawn up by the British Executive Committee on crude glycerin analysis and approved at a general meeting of crude glycerin makers, buyers and brokers held in London, on Oct. 3, 1912.

**Soap Lyes Crude Glycerin.**—Analysis to be made in accordance with the International Standard Methods (given above):

**Glycerol.**—The standard shall be 80% of glycerol. Any crude glycerin tendered which tests 81% of glycerol or over shall be paid for at a *pro rata* increase, calculated as from the standard of 80%. Any crude glycerin which tests under 80% of glycerol, but is 78% or over shall be subject to a reduction of  $1\frac{1}{2}$  times the shortage, calculated at a *pro rata* price as from 80%. If the test falls below 78% the buyer shall have the right of rejection.

**Ash.**—The standard shall be 10%. In the event of the percentage of ash exceeding 10%, but not exceeding 10.5% a percentage deduction shall be made for the excess calculated as from 10% at *pro rata* price and if the percentage of ash exceeds 10.5% but does not exceed 11% an additional percentage deduction shall be made equal to double the amount in excess of 10.5%. If the amount of ash exceeds 11% the buyer shall have the right of rejection.

**Organic Residue.**—The standard shall be 3%. A percentage deduction shall be made of 3 times the amount in excess of the standard of 3% calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 3.75%.

**Saponification Crude Glycerin.**—Analysis to be made in accordance with the International Standard Methods, 1911.

**Glycerol.**—The standard shall be 88%. Any crude glycerin tendered which tests 89% or over shall be paid for at a *pro rata* increase calculated as from the standard of 88%. Any crude glycerin which tests under 88%, but is 86% or over shall be subject to a reduction of  $1\frac{1}{2}$  times the shortage calculated at *pro rata* price as from 88%. If the test falls below 86% the buyer shall have the right of rejection.

**Ash.**—The standard shall be 0.5%. In the event of the ash exceeding 0.5%, but not exceeding 2.0%, a percentage reduction shall be made equal to double the amount in excess of 0.5%. If the amount of ash exceeds 2.0% the buyer shall have the right to reject the parcel.



(1) If the weight of the sugar is less than 0.05 grm., a few milligrams of barium hydroxide in excess of the sugar are added.

(2) If the weight of the sugar is between 0.05 and 0.3 grm., an equal weight of barium hydroxide is used.

(3) If the sugar is between 0.3 and 0.5 grm.,  $\frac{4}{5}$  of its weight of barium hydroxide is added.

The mixture is frequently shaken and after about 30 minutes some sand is added and the glycerol extracted by heating, first with 40 c.c., then 2 or 3 times with 25 c.c. of acetone. The solution after filtration is evaporated at a temperature below  $56^{\circ}$ , the residue being dried at 60 to  $65^{\circ}$  and weighed. The glycerin so obtained contains about 5 mg. of impurities which about compensates for loss in evaporation, etc.

**Estimation of Glycerol in Fats.**—Willstätter and Madinaveitia,<sup>1</sup> state that the drawbacks (due to incomplete hydrolysis) of the method of Zeisel and Fanto described in Vol. III, p. 461, when applied to fats, are obviated by using hydriodic acid of sp. gr. 1.8, with small quantities of the fat (0.15 to 0.35 grm.). About 0.2 grm. of the glyceride is treated with 10 c.c. of the hydriodic acid (sp. gr. 1.8) in Zeisel and Fanto's apparatus, the mixture being heated at  $110-115^{\circ}$  until the action starts; the temperature is then kept constant for 20-40 minutes, until the silver solution in the absorption flask becomes clear again, after which the heating is continued for 1 hour at  $130-140^{\circ}$ . The glycerol is then calculated from the amount of isopropyl iodide as in the original method. Results are given by the authors which show that when the method is carried out in the manner described, it possesses a very considerable degree of accuracy.

#### ERRATA IN VOL. II.

Page 461, line 11 from bottom, for "AgNo<sub>3</sub>" read AgNO<sub>3</sub>.

Page 475, line 13 from bottom, after "Mayrhofer," insert "see page 434."

Page 475, line 4 from bottom, for "Wainright" read "Wainwright."

<sup>1</sup> *Ber.*, 1912, 45, 2825.



# CHOLESTEROL.

By J. ADDYMAN GARDNER, M. A., F. I. C.

## ESTIMATION OF CHOLESTEROL IN ANIMAL TISSUES.

Various methods have been proposed in recent years for the accurate estimation of cholesterol and its esters in tissue extracts, but whatever the method adopted for this purpose, the accuracy of the estimation in the tissue itself must depend ultimately on the thoroughness with which the fats and lipoid substances are extracted from the tissue.

Pflüger<sup>1</sup> long ago showed that it was impossible to extract the whole of the fat from a dried tissue by simply extracting with ether in a Soxhlet apparatus and Dormeyer<sup>2</sup> proposed to get over the difficulty by digesting with pepsin and hydrochloric acid prior to the extraction with ether.

Kumagawa and Suto<sup>3</sup> and Schimidzu<sup>4</sup> find that the most certain method of extracting the whole of the fatty acids and unsaponifiable matter contained in a tissue is to destroy the tissue completely by heating with an alkali. Grigaut<sup>5</sup> carries this out in the following manner: 20 c.c. of blood serum are mixed with 20 c.c. of a solution of sodium hydroxide, containing 400 grm. NaOH per litre, and heated in an autoclave at 110° for 1 hour. In the case of solid tissues 5 to 10 grm. of the fresh tissue are heated in a similar manner with 40 c.c. of the soda solution diluted to half the strength.

The disadvantage of this method is that the cholesterol esters are saponified and therefore cannot be estimated. Kumagawa and Suto have, however, shown that the whole of the fats, etc., can be extracted from a tissue by boiling with absolute alcohol and they describe in their paper a convenient apparatus for the purpose.

For some years the writer has adopted the following method and obtained on the whole satisfactory results, so far as cholesterol is concerned. The *fresh* tissue is minced and ground to a fine pulp with fine sand. It is then mixed with 3 or 4 times its weight of plaster of Paris and allowed to set. The dry mass is then ground up again and extracted with ether in a Soxhlet for 2 or 3 weeks. On the whole it is better, particularly when time is a consideration, to extract first with hot alcohol for 1 hour, and then with ether for a day or so, especially in the case of serum, for in this substance the cholesterol appears to be more firmly held; and the writer now uses this method. In the case of liver, which contains enzymes which hydrolyse cholesterol esters, the

<sup>1</sup> *Archiv f. d. ges. Physiol.*, 1892, 51, 277.

<sup>2</sup> *Arch. f. d. ges. Physiol.*, 61, 341 and 65, 90.

<sup>3</sup> *Biochem. Zeitschr.*, 1904, 4, 186.

<sup>4</sup> *Biochem. Zeitschr.*, 1910, 28, 237-273.

<sup>5</sup> *Le cycle de la Cholestérolémie*, Paris, 1913.

tissue should be extracted as soon as possible after removal from the body, or else treated in such a way as to destroy the enzyme.

### Estimation of Cholesterol and Cholesterol Esters in an Extract.

*Method of Windaus.*—Windaus in 1909<sup>1</sup> discovered that cholesterol, but not esters of cholesterol, readily combines quantitatively with digitonin to form a highly insoluble digitonin-cholesteride, according to the following equation:



Digitonin-cholesteride is insoluble in water, acetone, ether, petroleum ether, ethyl acetate and benzene. 100 c.c. of ethyl alcohol (95%) dissolve at 18° only 0.014 gm., and at 78° C. about 0.16 gm.; 100 c.c. of 50% alcohol at a boiling temperature dissolve 0.03 gm. It is readily soluble in pyridine and slightly in methyl alcohol.

Digitonin-cholesteride readily dissociates on heating in the vapour of boiling xylene. The compound is placed in a paper thimble and suspended in a flask containing boiling xylene. After heating for 15 hours the dissociation is usually complete. The cholesterol dissolves in the xylene and the insoluble digitonin remains in the thimble and can be used again. The cholesterol is readily recovered by distilling off the xylene in steam.

For the quantitative estimation Windaus adopts the following plan:<sup>2</sup>

The ethereal or other extract of a tissue is evaporated and the residue taken up in 30 times its volume of hot 95% alcohol. This solution is treated with a 1% solution of digitonin in hot 90% alcohol so long as a precipitate is produced, care being taken to leave the digitonin in slight excess. After several hours the precipitate is filtered off on a Gooch crucible, and washed first with alcohol and then with ether. It is then dried at 100°–110° and weighed. Care should be taken in weighing as the compound is somewhat hygroscopic.

The filtrate from the digitonin-cholesteride is concentrated and after adding water is shaken out with petroleum ether or ether. The excess of digitonin remains in the aqueous alcoholic solution, whereas cholesterol esters, fats and other lipoids dissolve in the ethers. The petroleum or ether solution is divided into 2 parts, one serving for the isolation of the esters and the other for their quantitative estimation. For the latter purpose the petroleum or ether is distilled off, and the residue saponified by warming with alcoholic potassium hydroxide. The cholesterol set free is then shaken out with petroleum ether and estimated as above. This second precipitate gives the amount of combined cholesterol which was originally present as ester.

The writer's mode of procedure,<sup>3</sup> which was worked out before the appearance of Windaus' later paper, differs slightly in detail from that recommended by him.

<sup>1</sup> *Ber.*, 1909, 42, 238.

<sup>2</sup> *Zeit. physiol. Chemie*, 1910, 63, 110.

<sup>3</sup> Fraser and Gardner, *Proc. Roy. Soc.*, 1910, B, 82, 560.

After precipitating the alcoholic solution of the extract with a slight excess of digitonin in 95% alcohol, the mixture after standing some hours is evaporated to dryness in a vacuum desiccator. The precipitate is then washed by decantation with ether into a previously tared filter paper until the ethereal washings give no residue on evaporation. Care should be taken to use the minimum volume of ether possible. The excess of digitonin is then washed away by warm water. In most cases the filtration is tedious and it was often found more satisfactory to use a tared paper rather than a Gooch crucible, care being taken to subject the tare to exactly the same treatment as the filter paper which received the precipitate. The washing with water is continued until there is no residue on evaporation, or until the washings cease to froth on shaking. The precipitate is then dried in an air-oven at  $110^{\circ}$  and weighed in a stoppered bottle. In order to estimate the esters the ethereal washings containing the fat and esters may be saponified with sodium ethoxide in the manner described below. It was found preferable, however, when the amount of material available was sufficient, to divide the original extract into two halves. In one-half the free cholesterol is estimated as above and the other half is saponified and the total free and combined cholesterol again estimated. To saponify the esters the extract is dissolved in ether and a large excess of an alcoholic solution of sodium ethoxide added. The saponification of the esters is always complete on 24 hours' standing in the cold. The precipitated soaps are filtered and well washed with ether. The filtrate containing the total cholesterol is thoroughly washed by repeated shaking in a separator with water. The ethereal solution thus obtained is evaporated and the cholesterol estimated as above. Should it happen that the quantity of soap produced is large, it is necessary to allow the ether adherent to evaporate, grind the soap up with excess of salt and extract in a Soxhlet with ether. With small quantities of soap this is unnecessary.

The weight of digitonin-cholesteride  $\times 0.243$  gives the weight of cholesterol. For most purposes it is sufficient to take  $\frac{1}{4}$  the weight of the compound.

Both the methods of procedure described have given excellent results in the writer's laboratory. The digitonin method has been adversely criticised by various writers. It has been pointed out that errors are introduced owing to the slight solubility of the compound in ether or petroleum ether, and that this solubility may be increased if the ether already contains fat or other lipoid substances. When a fair quantity of the compound is weighed such errors are negligible, but become more serious as the quantity dealt with becomes smaller. Such errors are, however, inherent in every gravimetric method of analysis when the quantities to be estimated fall below a certain limit. When the quantity of cholesterol to be estimated is very small the writer measures the volume of ether used and makes a correction for the compound dissolved. It is better to make this correction by means of a control experiment with digitonin-cholesteride, keeping the conditions as similar as possible to those in the actual estimation. Similar insoluble digitonin

compounds are given by some other members of the sterol group, *e.g.*, bihydro-cholesterol, coprosterol, some phytosterols.  $\Psi$ -coprosterol and the non-crystalline sterol alcohols of faeces are not precipitated.

The comparative behaviour of the different members of the phytosterol group has not as yet been investigated.

**Method of Adrien Grigaut.**<sup>1</sup>—Grigaut employs a colorimetric method depending on Liebermann's reaction, viz., when cholesterol is dissolved in acetic anhydride and to the cold solution a drop of strong sulphuric acid is added, a succession of colours—red, blue, bluish-green and finally green—gradually appear. His mode of procedure in case of blood-serum is as follows: 2 c.c. of serum are placed in a small tap funnel with graduation marks at 15 c.c. and 30 c.c., alcoholic sodium hydroxide (1 in 200) are then added up to the 15 c.c. mark and finally ether to the 30 c.c. mark. The funnel is now stoppered and inverted several times to mix the contents thoroughly. After standing until the ethereal layer separates, the aqueous lower layer is run off and the ethereal solution washed twice by shaking each time with 20 c.c. of water. After draining off the wash water the ethereal solution is transferred to a porcelain dish and evaporated to dryness. The fatty residue is dissolved in 5 c.c. of chloroform and transferred to a graduated test-tube of 10 c.c. capacity. To this is now added 2 c.c. of pure acetic anhydride and 3 drops of a solution of sulphuric acid of 66° Bé. At the same time he introduces into a similar graduated tube 5 c.c. of a standard chloroform solution of cholesterol (containing 0.06 grm. per 100), 2 c.c. of acetic anhydride and 3 drops of acid. The tubes are allowed to stand for half an hour for the colour change to become stationary (green). 5 c.c. of the two coloured solutions are poured into the two tubes of a colorimeter, and the one with the deeper tint diluted with a mixture of chloroform, acetic anhydride and sulphuric acid in the above proportions until the tints in the two tubes are equal. If then  $n$  is the number of c.c. of the diluted solution, the amount of cholesterol  $P$  contained in a litre of serum is given by the following formula:

(1) In the case in which the solution to be estimated is diluted

$$P = 0.30 \times n \text{ grm.}$$

(2) In the case in which the standard solution is diluted

$$P = \frac{7.50}{n} \text{ grm.}$$

In order to estimate the cholesterol in a solid tissue, 0.2 to 1 grm. of the tissue, according to its cholesterol content, is put into a 90 c.c. flask with 30 c.c. of alcoholic sodium hydroxide (1 in 100) and heated on a water-bath until the tissue is dissolved and the volume of the mixture reduced to 15 c.c. The 15 c.c. of liquid are then introduced into the tap funnel described above and

<sup>1</sup> *Le cycle de la Cholestérinémie*, p. 28.

the flask washed with 15 c.c. of ether which is also added. The subsequent procedure is exactly the same as in the case of serum.

The weight  $P$  of cholesterol contained in 1 kilo of tissue will be obtained by the preceding formula in which the variable weight  $p$  of the tissue taken is introduced.

(1) In case in which the solution to be estimated is diluted

$$P = \frac{0.6 n}{p} \text{ grm.}$$

(2) In case in which the contents of the tube containing standard solution are diluted

$$P = \frac{15}{n \times p} \text{ grm.}$$

The method is open to the serious objection that the Liebermann reaction is a progressive one and the time taken to arrive at a given tint will depend on the amount of cholesterol present. Experience, however, shows that when the percentages of cholesterol do not differ very markedly, as for instance in different sera, good comparative results are obtained. Owing to the small quantities of material taken the error must be considerable when the units are multiplied up to 1,000 c.c. or 1 kilo.

The method gives only the total cholesterol and does not permit of differentiation between free cholesterol and its esters. The most serious objection to the method is that the Burchard-Liebermann reaction is given by other substances than cholesterol, among which may be mentioned cholesterol esters, hydroxycholesterol, coprosterol, etc., and the reagent gives coloured solutions with resins and other substances not belonging to the sterol group.

Leonhard Wacker<sup>1</sup> has moreover recently shown that human fat contains in addition to cholesterol, another substance of the sterol group, which is obtained along with the cholesterol in the unsaponifiable matter. This substance constitutes a very considerable part of the lipoid matter dissolved in fat. It is a wax-like compound, melting at 25°–32°, and gives colour changes with the Liebermann reagent, but is not precipitated by digitonin.

The writer has also recently isolated similar substances from human fæces. They are readily obtained from the unsaponifiable matter of fæces, after the bulk of the coprosterol has been removed by crystallisation from acetone and the last traces precipitated as digitonin compound, by distilling in superheated steam and subsequently fractionating in a high vacuum. They give a reaction with Liebermann's reagent, but are not precipitated by digitonin.

Though the colorimetric method gives useful results with sera, results by this method are of little value in the case of solid tissues.

#### ERRATA IN VOL. II.

Page 484, line 11 for "incholesteryl" read "ischolesteryl."

Page 487 line 7 from bottom, for " $(\alpha)_D$ " read " $[\alpha]_D$ ."

<sup>1</sup> *Zeit. f. physiol. Chemie*, 1912, 80, 404.

# WOOL, GREASE AND CLOTH OILS.

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By AUGUSTUS H. GILL.

The nature of the hydrocarbons obtained from distilled wool-grease (Vol. II, p. 503) has been investigated by Gill and Forrest.<sup>1</sup> They were found to be olefines boiling at 110° to 193° under 1 mm. pressure and having formulæ corresponding to C<sub>20</sub>H<sub>40</sub> (eicosylene) to C<sub>30</sub>H<sub>60</sub> (triacontylene). They were white crystalline substances resembling paraffin; some oily lower boiling compounds were also observed.

## ERRATA IN VOL. II, INDEX.

Page 515, for "Amidol" read "Arnidiol."

Page 515, for "Caratol" read "Carotol."

Page 516, for "Electric Conduct" read "Electric Conductivity," "Singili" read "Gingili," "Hydrocaratol" read "Hydrocarotol."

<sup>1</sup> *J. Amer. Chem. Soc.*, 1910, 32, 1071.

# HYDROCARBONS

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By R. LESSING, PH.D.

Hydrocarbons occur in nature ready formed in natural gas, petroleum oil, earth-wax, shale and coal, or are obtained from these and a great number of vegetable substances by ordinary or destructive distillation. The fact that these natural products as well as the distillates obtained from them consist invariably of mixtures, mostly of a highly complex character, renders the identification and estimation of individual compounds exceedingly difficult, and in many cases practically impossible. The analyst is therefore confronted in many cases with problems which have so far not been solved satisfactorily.

## Physical Methods of Separation.

Fractional distillation offers a means of separating groups possessing similar physical characteristics within certain narrow limits. But even where hydrocarbons of one series, such as paraffin or benzene derivatives are concerned, their quantitative isolation is a very lengthy and tedious operation involving many fractionations on account of the close proximity of the boiling points and the consequent overlapping of fractions. The problem becomes, however, still more complex when hydrocarbons of different series are present, and inseparable mixtures of constant boiling point are formed. Thus, the addition of aliphatic to aromatic hydrocarbons exerts a depressing influence and a small addition of *n*-hexane may lower the boiling point of benzene to 65°.¹

A further difficulty is introduced by the instability of the higher members at the temperature at which they boil; distillation is then accompanied by decomposition or molecular changes ("cracking") and must be carried out at reduced pressure or with the aid of superheated steam.

Notwithstanding these limitations, distillation is an indispensable method in examining hydrocarbon mixtures, both for the determination of the boiling range without fractionation of the distillates and for the separation of fractions boiling within more or less narrow limits. The latter operation, by which such complex mixtures as crude petroleum oil or coal tar are resolved into groups of comparative simplicity, almost invariably precedes the application of specific chemical reagents.²

¹ Jackson and Young, *Trans.*, 1898, 73, 922.

² For a closer study of the subject see Sydney Young, "*Fractional Distillation*," London, 1903.



The range and number of fractions to be taken depends on the scope of the examination and may vary between wide limits. The sp. gr. of each fraction is determined, and often the refractive index, optical rotation, viscosity, flash point, etc., will give useful information.<sup>1</sup>

Fractional distillation—at low temperatures—can also be applied to hydrocarbons which are gaseous at ordinary temperature and pressure. Lebeau and Damiens<sup>2</sup> cool mixtures of the lowest members of the paraffin series and hydrogen, to the temperature of liquid air, where methane has still a tension of 80 mm. of mercury whilst the higher members are liquid. The gaseous portion is separated, measured and analysed and the condensate is successively fractionated from baths of solid carbon dioxide and acetone, and petroleum ether cooled by liquid air, yielding binary mixtures of ethane and propane, propane and *iso*-butane, the components of which can be estimated by combustion.

An apparatus has been devised by which the constituents of such complicated mixtures as coal gas can be accurately determined in a practical way, largely by the aid of fractional distillation.<sup>3</sup>

Amongst other physical methods of separating hydrocarbons, filtration or diffusion through Fuller's earth, bone charcoal and other porous materials, has little importance from the point of view, of general analysis but "cold fractionation" by solution or precipitation is of value in certain cases. S. Aisinmann<sup>4</sup> studied the solubility of Russian petroleum distillates and residues in alcohol. Alcohol is added from a burette to 10 c.c. of the oil at ordinary temperature, until complete solution takes place. Solubility decreases with a rise in boiling point. With heavy oils it is necessary to shake with an excess of alcohol and decant the alcohol solution repeatedly until an insoluble residue remains behind. Hydrocarbons rich in carbon require more alcohol for solution, but dissolve, on the other hand, less alcohol, than those poorer in carbon, a fact conducive to good separation.

Fractional precipitation can be effected according to Charitschkoff<sup>5</sup> by

<sup>1</sup> A distillation method for the estimation of toluene in commercial toluol, solvent naphtha, and other coal-tar distillates has been devised by H. G. Colman (*J. Gas Lighting*, 1915, 129, 196, 314) while this article was in the press.

The principle of the method is to estimate the volume of the portions boiling below 105° and above 117°, by which figures the toluol percentage can be ascertained from an empirically constructed table. It is necessary to prepare the sample by a careful distillation up to 145° using a Young 12-bulb "pear" fractionating column, and to add to the distillate definite quantities of pure benzene, toluene, and xylene in order to bring the expected percentage of toluene within the range of from 50% to 75% for which only the table is correct. Corrections for paraffin contents are made by ascertaining the sp. gr. of the fraction 105° to 117° and deducting 0.75% toluol for every 0.001 that the sp. gr. is found below 0.868 from the total toluol contents of the mixture.

Another method for the same purpose but only applicable to comparatively pure toluols has been proposed by D. Northhall-Laurie (*Analyst*, 1915, 40, 384). He distils 200 c.c. of the sample at a uniform rate collecting the first quarter as distillate and leaving the last quarter in the distilling flask. The boiling points of these two fractions are ascertained in a special apparatus and the results plotted on a graph, from which the percentage can be read off directly. The graph is also available for estimating benzene and xylene, in commercial toluols.

For both methods it is necessary to consult the original publications as they largely depend for their accuracy on the strict observance of manipulative details, as well as on the empirical tables.

<sup>2</sup> *Compt. rend.*, 1913, 156, 144, 325.

<sup>3</sup> See also G. A. Burrell and J. W. Robertson, *J. Ind. Eng. Chem.*, 1915, 7, 17, 112.

<sup>4</sup> *Dingl. pol. J.*, 1895, 297, 44.

<sup>5</sup> *Chem. Zeit.*, 1904, 287, 87.

dissolving petroleum oils in amyl alcohol and separating the fractions successively by the addition of ethyl alcohol in small portions.

For the removal of oxygen- and sulphur-containing asphaltic compounds from hydrocarbon oils Holde's<sup>1</sup> method is widely used. From 5 to 20 grm. oil are well shaken in a clear glass bottle with 40 volumes of "Normal" benzin (sp. gr. at 15° C. 0.695–0.705; boiling from 65° to 95° C.; free from unsaturated and benzene hydrocarbons). After standing for 24 hours at a temperature of from 15° to 20° C. protected from direct sunlight, the solution is filtered through a double filter and the residue washed with the same benzin until a drop of the filtrate leaves no oily residue on evaporation. The benzin solution then contains only the hydrocarbon oil. The asphaltic residue may be dissolved in coal tar benzene and, after evaporation of the latter, weighed (compare Vol. III, p. 54).

By this method only the hard asphalt is removed. Soft asphalts can be separated by dissolving the oil in 25 volumes of ethyl ether and adding to the solution, drop by drop and with continual shaking, 12.5 volumes of 96% (by weight) alcohol. After 5 hours' standing the precipitate is filtered and washed with a mixture of ether and alcohol in the same proportions (1:2) until 20 c.c. of the filtrate leave on evaporation no oily residue but only traces of a pitchy substance. The precipitate is dissolved in benzene and, after evaporation of the latter, weighed. If it is light in colour and likely to contain paraffin wax, this is separated by treatment with absolute alcohol in an extracting apparatus, preferably after mixing it with sand or alcohol extracted charcoal.

F. Schwarz<sup>2</sup> uses butanone (methyl-ethyl-ketone) which has been saturated with water, in which hydrocarbon oils are soluble and asphaltic bodies insoluble, in the place of either of the two preceding reagents, thereby obtaining hard and brittle asphalt residues (for details see page 246).

The estimation of solid paraffin in a petroleum distillate (boiling above 300° C.) is also based on a method of fractional solution. 5–10 grm. of an oil, or 0.5–1.0 grm. of a solid paraffin are dissolved at room temperature in a mixture of equal parts of ethyl ether and absolute alcohol; the temperature is then lowered to –20° C. and more ether-alcohol added so that all oily portions are kept in solution and only flakes of paraffin remain suspended. Oils containing much paraffin should be first dissolved in ether, the alcohol being added subsequently. The paraffin is filtered by suction on a funnel surrounded by a cooling mixture, washed with cooled ether-alcohol and then dissolved with hot benzene and, after evaporating the solvent and drying at 105° C., weighed. In view of the not inappreciable solubility of paraffin in the ether-alcohol mixture, a correction is made by adding to the result 0.2% for perfectly clear oils, 0.4% for semi-solid masses, and 1.0% for solid paraffins.

A method which must be classed amongst methods of fractional solution,

<sup>1</sup> *Unters. der Kohlenwasserstofföle und Fette*, Berlin, 1913, page 42.

<sup>2</sup> *Chem. Zeit.*, 1911, 35, 1417.

has been devised by Eldeleanu<sup>1</sup> who extracts aromatic and other unsaturated hydrocarbons from petroleum distillates by means of liquid sulphur dioxide at low temperature. The process is practised as a works operation on the large scale for refining lamp oils, but can also be used in the laboratory. If a petroleum distillate is mixed with liquid sulphur dioxide this is at first dissolved, but later 2 layers are formed, the lower one being a solution of the hydrocarbons of high carbon content in sulphur dioxide, whilst some of the gas is dissolved in the upper layer of paraffins or naphthenes. A special burette is used having stopcocks at both ends which by clips are prevented from being forced out. The oil to be tested is cooled in the burette to  $-10^{\circ}$  C., liquid sulphur dioxide is then added (which by its own evaporation cools itself to the same temperature) until the 2 layers are just forming. One-third of the volume of the lower is added in excess, the burette is then shaken and allowed to stand until separation is complete. The extract is run off, and the operation repeated twice with more sulphur dioxide. The bulk of the gas is allowed to evaporate in the air from both fractions and these are finally washed with water. No appreciable chemical action of the sulphur dioxide on the hydrocarbons takes place, but sulphur compounds are acted upon.

**Chemical Methods.**—The difficulties attached to the physical methods of separation apply almost in the same degree to the chemical treatment of hydrocarbon mixtures. Most specific reagents do not enable the analyst to identify or isolate individual compounds but act only as group reagents. There is also, as in the case of the physical examination, always a tendency of different groups overlapping. For instance, concentrated sulphuric acid which is frequently used to remove unsaturated compounds from saturated hydrocarbons is—contrary to statements in most text-books—capable of attacking paraffin hydrocarbons on prolonged contact and particularly when containing some sulphuric anhydride; a nitrating mixture, the typical reagent for aromatic hydrocarbons, will also attack naphthenes,<sup>2</sup> and similar examples can be found with nearly all the usual reagents.

It is important to remember that nearly all commercial hydrocarbon products, unless highly refined, contain members of different series; thus petroleum oils from practically any source contain besides aliphatic or naphthene (polymethylene) hydrocarbons, benzene homologues sometimes up to 40%;<sup>3</sup> on the other hand coal tar, especially in its lower fractions, comprises a number of aliphatic hydrocarbons. Shale oil distillates are mixtures of chain and cyclic compounds, and spirit from "cracked" oils which is likely to attain commercial importance in the near future, comprises a variety of hydrocarbons of varying degree of saturation.

Although the fact of hydrocarbons of different types frequently appearing

<sup>1</sup> Engler und Ubbelohde, *Zeit. angew. Chem.*, 1913, 26, I, 177.

<sup>2</sup> According to Worstall (*Amer. Chem. J.*, 1898, 20, 202) normal hexane yields some of the primary nitro-compound when boiled with nitric acid during a long period.

<sup>3</sup> Jones and Wootton, *J. Chem. Soc.*, 1907, 91, 1146; J. Steuart, *J. Soc. Chem. Ind.*, 1900, 19, 986.

together seems to justify a *prima facie* case for a systematised series of tests, no such scheme of general applicability has ever been devised. The kind of reagents employed and the sequence of operations must vary according to circumstances. Generally it will be found useful to proceed in this order: unsaturated aliphatic (olefines, acetylenes) and partially saturated hydro-aromatic compounds, aromatic compounds, naphthenes, paraffins. In most cases commercial requirements will not entail a complete examination of a hydrocarbon mixture, but only definite tests for certain properties or components will be specified.

**Olefines.**—The estimation of olefines by means of their bromine absorption, by which at any rate comparable values can be obtained, has been dealt with at length under this heading in Vol. III.

In order to distinguish between added and substituted bromine which will both be covered by the bromine absorption of, say, a mixture of olefines and aromatic hydrocarbons, Parker C. McIlhiney<sup>1</sup> estimates the hydrogen bromide formed in the latter case.

The sample is dissolved in 10 c.c. of carbon tetrachloride in a glass-stoppered bottle and 20 c.c. of *N*/3-bromine solution in the same solvent are added. After a few minutes 20 to 30 c.c. of a 10% solution of potassium iodide are added, care being taken that no bromine is lost; if necessary the mixture must be cooled and the stopper and neck of the bottle wetted with potassium iodide solution. The bottle is then shaken to ensure the absorption of the bromine and hydrogen bromide by the aqueous solution. The iodine present is now titrated with *N*/10-sodium thiosulphate. By then adding 5 c.c. of a neutral 2% solution of potassium iodate, a quantity of iodine equivalent to the hydrogen bromide formed is liberated and on titrating this, the bromine solution figure may be calculated. All solutions should be tested for acidity and a blank test made. Whilst addition of bromine is instantaneous, the amount of substitution is somewhat affected by the time of contact.

The bromine absorption may not only serve for the estimation but also for the removal of unsaturated from saturated hydrocarbons, which can be separated by distillation from the higher-boiling bromo-compounds.

Sometimes the iodine number is determined in preference to the bromine absorption. For this purpose the employment of Wijs' method is advisable and preferable to that of Hübl. In the case of crude distillate it is necessary to remove any hydrogen sulphide that may be present by shaking with a solution of lead acetate.<sup>2</sup>

A simple method of estimating unsaturated aliphatic or hydro-aromatic hydrocarbons in general consists in shaking the mixture repeatedly in a burette with 10 to 30% by volume of concentrated or fuming sulphuric acid until the volume shows no further reduction. The loss of volume indicates the

<sup>1</sup> *J. Amer. Chem. Soc.*, 1899, 21, 1084.

<sup>2</sup> *Gracie, Zeit. angew. Chem.*, 1905, 18, 1580.

percentage of unsaturated compounds. Heating must be avoided and if aromatic or naphthene hydrocarbons are present, the acid must be added very carefully to avoid a violent action, as these are sulphonated at high temperature by concentrated, and even at slightly raised temperature by fuming sulphuric acid.

A qualitative test for olefines by means of mercuric acetate has been devised by Balbiano and Paolini.<sup>1</sup> 3 to 4 c.c. of a hydrocarbon mixture are shaken with 10 c.c. of a saturated solution of this salt. If olefines are present a deposit of white crystals will be observed after 24 hours.

Tausz<sup>2</sup> based a method for the estimation of olefines on this behaviour. 50 c.c. of the hydrocarbon mixture are shaken with 150 c.c. of mercuric acetate solution for 5 minutes and heated with it for 3 hours under a reflux; the product is then steam distilled, all operations carried out in the same, specially designed flask. The distillate is washed with dilute sodium hydroxide solution and then with sodium hydrogen sulphite solution to remove acetic acid, aldehydes and ketones respectively. The remaining portions are the saturated hydrocarbons. The unsaturated portion can be recovered by decomposing the complex mercury salts with dilute hydrochloric acid.

For the estimation of gaseous olefines, Lebeau and Damiens<sup>3</sup> proposed the use of a 1% solution of vanadium pentoxide in concentrated sulphuric acid or of a 6% solution of uranyl sulphate in the same acid. Either of these solutions will take up 150 times its volume of ethylene very rapidly.

The formation of complex mercury salts is also used by these authors to estimate acetylene. A solution containing 25 grm. of mercuric iodide and 30 grm. of potassium iodide in 100 c.c. of water is capable of absorbing 20 times its volume of acetylene. On making the solution alkaline, a white precipitate of the complex salt is formed. They claim that olefines do not react and can be separated from acetylene by this method, but this appears to be doubtful in view of the above-described action of mercuric acetate on olefines.

**Aromatic Hydrocarbons.**—In view of the commercial importance of coal-tar derivatives, the hydrocarbons of the benzene series have been studied more closely than others, and partly for that reason and partly on account of their properties it is less difficult to isolate and identify individual members of the series.

Sulphonation of aromatic hydrocarbons by heating them with concentrated or fuming sulphuric acid has been mentioned above. From the sulphonic acids thus produced and separated from mixtures, the hydrocarbons may be recovered by distillation in superheated steam.

A more general and useful method by which aromatic hydrocarbons may be

<sup>1</sup> *Chem. Zeit.*, 1901, 25, 932, *Ber.*, 1902, 35, 2994; see also K. A. Hofmann and J. Sand, *Ber.*, 1900, 33, 1340, 1353; 1901, 34, 2906; Denigès, *Bull. Soc. chim.*, 1898 [3], 19, 494.

<sup>2</sup> Dissertation, Karlsruhe, 1912.

<sup>3</sup> *Compt. rend.*, 1913, 156, 557.



recognised and isolated from mixtures is nitration. The carefully fractionated hydrocarbons are treated with 2 to 5 times their volume of a nitrating mixture consisting of 1 volume nitric acid (sp. gr. 1.45–1.50) and 1.5 to 2 volumes of sulphuric acid (sp. gr. 1.85). With good stirring or shaking, careful mixing and low temperature, mostly mono- and di-nitro-products are formed. At higher temperature or with great excess of acid, tri-nitro-compounds will be formed.

When no further action takes place, the nitration is completed and the mixture separates into 3 layers. The acids form the bottom layer, the nitro-compounds are in the dark-brown middle layer, and the unattacked hydrocarbons in the upper layer. The two upper layers are soluble in each other to a certain extent. The acids are either separated first or after dilution with water. The hydrocarbons and nitro-products are washed with water and a little sodium carbonate solution, and are separated by distillation with or without steam. The nitro-compounds, if solid, can be identified by their melting points, or else by reduction to their amines and possibly the conversion of the latter into acyl derivatives or salts.

Formaldehyde, which although of fairly general applicability is not yet being employed to the extent which it deserves in hydrocarbon analysis, was suggested for this purpose by A. Nastjukoff in 1904.<sup>1</sup> He found that a mixture of concentrated sulphuric acid and formaldehyde solution reacts with all unsaturated cyclic hydrocarbons forming insoluble compounds, termed "formolite." Neither saturated hydrocarbons of any kind nor unsaturated chain hydrocarbons show this behaviour, but all aromatic and partially saturated hydro-aromatic hydrocarbons, as well as terpenes and hydroterpenes, yield "formolites."

The sample is mixed with its own volume of concentrated sulphuric acid and half its volume of a 40% formaldehyde solution is then slowly added, the mixture being well cooled the whole time. (If the yield of "formolite" is higher than 50%, the ratio of sample, sulphuric acid and formaldehyde to be taken is 1:2:1.) It is then shaken until the temperature no longer rises. In many cases, particularly with viscous oils, it is advisable to dilute the sample previously with light petroleum spirit free from "formolite" yielding hydrocarbons. After half an hour's standing, the mixture is poured into ice water, the flask being washed out with water. An excess of ammonia is added to the acid solution and the precipitate is filtered and washed on a vacuum filter. The precipitate from heavy oils is first washed with petroleum spirit to remove unattacked oil, then with water until free from ammonia and is then dried at 105° C. In view of the difficulty of filtration and washing, it is sometimes necessary to repeat the extraction with spirit and water of the dried and powdered precipitate.

Nastjukoff calls the number of grams of precipitate per 100 c.c. of original

<sup>1</sup> *J. Russ. Chem. Phys. Soc.*, 1904, 36, 881; 1910, 42, 1596.

oil the "formolite number" of the oil or hydrocarbon mixture. The precipitates are of yellow to brown colour and practically insoluble in the usual solvents except to a small extent in chloroform.

The composition of the "formolites" is not yet cleared up; the unsaturated cyclic hydrocarbons combined with formaldehyde are equal to about 80% of the "formolite." V. F. Herr<sup>1</sup> proposed the use of methylal in place of formaldehyde on account of its solvent power for oils.

Naphthalene is now universally estimated by the picrate method. Some useful results were obtained by W. P. Jorissen and J. Rutten<sup>2</sup> in an investigation on the conditions of solubility of picric acid, naphthalene and naphthalene picrate. They found on the basis of the phase rule that for a complete conversion of the hydrocarbon into its picrate, it is necessary that the aqueous solution of picric acid employed should be supersaturated and in fact a certain amount of crystals should be present as a bottom body. A solution made by adding 100 c.c. of water to 2.7 gram. of pure picric acid will fulfil this condition. The usual alkalimetric estimation of the picric acid excess, by *N/10* sodium hydroxide, may be replaced by an iodometric method. 25 c.c. of a solution of potassium iodide and iodate (150 gram. KI, 30 gram. KIO<sub>3</sub>, 400 c.c. H<sub>2</sub>O) are added to 100 c.c. of the picric acid solution and are titrated with *N/10* thiosulphate solution and starch as indicator. The colour change is then more distinct than that of the phenolphthalein in the alkali titration<sup>3</sup> (see also page 266).

**Naphthenes (Polymethylenes).**—After removal of the unsaturated aliphatic and the aromatic hydrocarbons from a mixture, the polymethylenes and paraffins remain. Their separation is particularly difficult on account of the similarity of their physical and chemical characteristics. Specific gravity and refractivity will give some indication for their differentiation; generally qualitative tests will meet the case.

#### PHYSICAL PROPERTIES OF THE SIMPLEST CYCLOPARAFFINS.<sup>4</sup>

Name	M. p.	B. p.	<i>d</i> <sub>4</sub> <sup>o</sup>	<i>n</i>
Cyclopropane.....	−126.0°	about −35°	.....	.....
Cyclobutane.....	liquid at −80°	11.0–12.0°	0.7038	1.37520
Cyclopentane.....	liquid at −80°	49°	0.7635	1.40855
Cyclohexane.....	+ 6.4°	81°	0.7934	1.4266
Cycloheptane.....	.....	117.0–117.5°	0.8252	1.44521
Cyclooctane.....	+ 11.5°	145.3–148.0°	0.850	1.45777
Cyclononane.....	.....	170.0–172.0°	0.785	1.4328

Hydrocarbons of the polymethylene series are not attacked by a mixture of sulphuric and nitric acids at the ordinary temperature, nor readily on moderate heating.<sup>5</sup> With fuming nitric acid the behaviour of pentamethylene

<sup>1</sup> *Chem. Zeit.*, 1910, 34, 893. See also Severin, *Chem. Zeit.*, 1910, 34, 840.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1909, 28, 1179.

<sup>3</sup> E. Schlumberger, *J. f. Gasbel.*, 1912, 55, 1260.

<sup>4</sup> R. Willstätter and J. Bruce, *Ber.*, 1907 40, 3981.

<sup>5</sup> Francis and Young, *Trans.*, 1898, 73, 928.



and hexamethylene differs widely from that of their methyl derivatives, for the former are only attacked when heated and yield chiefly the corresponding dibasic acids—glutaric and adipic acids—whilst the methyl derivatives and especially methylpentamethylene, are acted on rapidly at the ordinary temperature with evolution of heat and for the most part broken down.

If heated with dilute nitric acid in sealed tubes, the polymethylenes yield according to Konowaloff<sup>1</sup> mono-nitro-compounds which are of tertiary character if the original hydrocarbon has a side chain. 5 c.c. of the hydrocarbon are heated in a sealed tube with 25 c.c. of nitric acid of sp. gr. 1.025 to 1.075 for 12 hours at 120° to 130°. The product is washed with sodium carbonate solution and water and dried with calcium chloride. The unattacked hydrocarbon is distilled off. If the distillation is carried out under reduced pressure, it can be continued until the nitro-compounds are carried over. Secondary nitro-compounds are separated from the tertiary by extraction of the mixture with alcoholic or dilute aqueous potassium hydroxide.

Polymethylenes may be qualitatively tested by de-hydrogenating them according to Sabatier's method. Cyclohexanes are converted into aromatic hydrocarbons by passing them over finely divided and freshly reduced nickel at 300° C. and can then be easily identified by the formol reaction.

Zelinsky<sup>2</sup> converted *cyclohexane* quantitatively into benzene and hydrogen by passing it 3 times very slowly over palladium black at 300° C.

In this connection mention may be made of S. Fokin's<sup>3</sup> proposal to estimate the degree of unsaturation of organic compounds by the determination of the "hydrogen number," *i.e.*, the number of c.c. of hydrogen (at 0° C. and 760 mm.) which are absorbed by 1 gram. of the substance when submitted to hydrogenation. A distillation flask (50 to 150 c.c.) having a small beaker fused inside on the bottom is connected by means of the side tube to a gas burette and a gas holder containing hydrogen. In the small beaker are placed 0.1 to 0.2 gram. of molecular platinum moistened with 0.25 to 0.5 c.c. of water, and in the flask the substance to be examined and 20 to 30 c.c. of alcohol free from dissolved oxygen. The flask is shaken by a shaking machine and the hydrogen absorbed is read off when constancy is obtained.

Willstätter<sup>4</sup> had previously hydrogenated polymethylenes by means of Sabatier and Senderens' method.

A method for the estimation of the total hydrogen contained in a substance is due to A. P. Lidoff.<sup>5</sup> From 0.25 to 0.5 gram. of the substance is mixed with about 1 gram. of powdered magnesium, which has been ignited previously in a current of hydrogen and the mixture is introduced into a thick-walled test-tube made out of combustion tubing. This tube should

<sup>1</sup> Ber., 1895, 28, 1863., Chem. Zentr., 1898, i, 926; 1899, i, 966; 1902, i, 564.

<sup>2</sup> Ber., 1911, 44, 3121.

<sup>3</sup> Russ. Phys. Chem. Soc., 1908, 40, 700.

<sup>4</sup> Loc. cit.

<sup>5</sup> J. Russ. Phys. Chem. Soc., 1907, 39, 195, 208. Zeitsch. anal. Chem., 1907, 46, 357.

be 130 mm. long and 9 mm. in diameter; a layer of magnesium powder is placed above the mixture so as to fill the tube to a height of about 80 mm. After connecting the open end of the tube with a gas measuring burette, the layer of magnesium is heated to redness and the heat is then gradually extended to the lower part of the tube containing the mixture. The usual precautions are taken in adjusting the zero of the burette and in reading the volume of the hydrogen.

The method has been applied by the author to the examination of hydrocarbon oils.

**Paraffins.**—The paraffins possessing the smallest reactivity remain behind after removal of all the other hydrocarbons. They are, however, liable to be attacked by strong fuming sulphuric acid on prolonged heating. Whilst practically unattacked by nitric acid in any form at ordinary temperature, the normal members may be slowly decomposed by fuming nitric acid, when heated on the water-bath; but the iso-paraffins are readily attacked under these conditions, a moderate yield of nitro-compounds being obtained.<sup>1</sup>

The estimation of solid paraffin in oils by the ether-alcohol method has been described. It is frequently necessary to estimate conversely the amount of oil in a solid paraffin.

Thus Marcusson<sup>2</sup> bases the identification of a paraffin wax, according to its origin, upon the residual oil which it always contains. 100 *gram.* paraffin are dissolved in 300 c.c. of ethyl ether and the same volume of ethyl alcohol (96%) is then added; the mixture is cooled in running water and filtered on a Büchner funnel. The filtrate is evaporated again, dissolved in 50 c.c. of ether and precipitated with 50 c.c. of alcohol, cooled to  $-20^{\circ}\text{C.}$ , filtered and evaporated. The iodine number is determined of the oily residue which may be taken up in benzin for further purification. This is from 3 to 12 with petroleum paraffins and from 18 to 21 with shale paraffins; but similar differences are observed before and after refining with samples of the same origin.

F. Sommer<sup>3</sup> makes use of the formaldehyde method for the same purpose. 20 *gram.* of paraffin are melted in a flask, 20 c.c. of concentrated sulphuric acid are first added and then gradually 20 c.c. of formaldehyde solution, the flask being shaken and excessive heating avoided. The mixture becomes dark red and is left for 20 minutes on the water-bath; it is then turned into a porcelain basin and left on the water-bath until the paraffin is completely separated. After cooling, the paraffin cake is lifted off, the acid liquid is diluted with water and the "formolite" is shaken out with chloroform. The chloroform solution is evaporated and the residue dried

<sup>1</sup> Francis and Young, *loc. cit.*

<sup>2</sup> *Zeit. angew. Chem.*, 1910, 23, 1057.

<sup>3</sup> *Petroleum*, 1912, 7, 409.

at 105° C. The "formolite" varies from 0.02 to 1.55% and corresponds with the tendency of a paraffin to turn yellow.

F. Epstein and H. Polonyi<sup>1</sup> employ the formation of picrates for the same purpose. 20 gm. of paraffin are melted at low temperature, 0.02 gm. picric acid is added and well stirred in; after allowing the insoluble matter to settle, the paraffin is poured into a mould of tinplate which floats on ice water. The colour of the solidified cake is compared with a standard sample and 0.05% of oil in paraffin can be estimated.

<sup>1</sup> *Petroleum*, 1912, 7, 594.

# BITUMENS.

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By S. S. SADTLER.

Bituminous substances, according to Herbert Abraham, are classified as (1) natural and (2) artificial. The natural are bitumens and pyrobitumens. The bitumens are (a) *gaseous*, as natural and marsh gas; (b) *liquid*, as petroleums with paraffin, asphaltic or mixed bases, or malthas ("mineral tars"); (c) *solid*, as mineral waxes like ozokerite (ceresin), montan wax and hatchettite, or mineral pitches like pure, calcareous, siliceous and earthy asphalt(um), or asphaltites like gilsonite, glance pitch, manjak, grahamite. The pyrobitumens are (a) solids occurring fairly pure, such as elaterite (wurtzelite), albertite, impsonite, derived from asphalts, and peat, lignite, bituminous and anthracite coals derived from vegetable growth; (b) solids in which mineral materials predominate, such as bituminous shales and schists. The artificial bituminous substances may be of (1) *animal origin*, as bone tar and bone tar pitch from bones, or fatty acid pitches from animal and vegetable fats, such as stearin pitch (candle tar), cotton-oil-foots pitch, wool-fat pitch, palm-oil pitch, cottonseed-oil pitch; (2) *vegetable origin*, as fatty acid pitches from vegetable oils, resin pitch from saps of *Coniferae*, pine tar and pine tar pitch from wood and roots of *Coniferae*, wood tar and wood tar pitch from the hard woods; (3) *mineral origin*, as water gas tar and pitch, sludge pitch, petroleum asphalt (petroleum pitch), blown (oxidized) petroleum asphalt from petroleum; asphalt(um) from malthas, paraffin, etc., from ozokerite, etc., peat tar and pitch from peat, lignite tar (brown coal tar) and pitch from lignite (brown coal), coal tar and pitch, coke oven tar and pitch, blast-furnace tar and pitch, water-gas tar and pitch, generator-gas tar and pitch from bituminous coal; elaterite pitch from elaterite, shale oil and shale oil pitch from bituminous shales.

## Asphalt.

**Method of Analysis of Total Bitumen in Surface Mixtures.**—Weigh 10 grm. in a long tube or deep glass cup with ground stopper and then fill  $\frac{3}{4}$  full with carbon disulphide. Whirl in a centrifuge for several minutes. Decant the solvent into a tared platinum dish and fill the tube  $\frac{3}{4}$  full with fresh carbon disulphide. Stir sediment with a rod and whirl again. This is repeated until the solvent above the sediment remains colourless.

Ignite these extracts in a good draught and burn to an ash. Dry the test-tube with the sediment and weigh. Add correction in the platinum dish and subtract from 100% to obtain the bitumen.

**Method of Extracting Bitumens from Binding Courses, Topekas, Etc.—**

A special extractor (New York Testing Laboratory Type, see Figs. 10 and 11), for analysis of paving mixtures containing broken stone, is used. The bituminous mixture should be warmed until it can be readily broken apart by hand, without fracturing any of the stony particles; 500 grm. of the disintegrated mixture should be packed as tightly as possible in the wire basket and then covered with a disc of cotton or felt of  $\frac{1}{4}$  to  $\frac{1}{2}$  in. thick; 175 to 200 c.c. of carbon disulphide, carbon tetrachloride, chloroform or

FIG. 10.—N. Y. testing laboratory extractor in parts.

benzol are placed in the inside vessel in which the wire basket is suspended. Cool water should be circulated through the inverted cone condenser which is also the cover of the apparatus and not intended to fit tight. A 16 c.p. carbon filament incandescent lamp is the source of heat. A 500 grm. sample of the mixture should be extracted clean with carbon disulphide in about 3 hours. From 200 to 300 grm. of asphalt block or Topeka type mixture is a sufficiently large sample for that type of material. After extraction, the solvent and matter removed from the sample during the analysis should be burnt to recover any fine mineral particles which may have passed into the extract. The extractors are made entirely of metal.

**Ductility (New York Testing Laboratory Methods).—**The sample is melted and poured into brass briquette moulds,<sup>1</sup> the latter first having been amalgamated to prevent the asphalt from adhering. The sample is then cooled and placed in ice water (41° F.) for 15 minutes. Then with a heated knife, the excess of asphalt over 1 cm. thickness is cut off so that the centre and narrowest portion of the briquette is 1 sq. cm. The briquette is placed in water at 77° for 15 minutes, and then drawn out in water at 77° F. in a ductility machine, so regulated that it only moves 5 cm. per minute. The reading on the metre rule when the thread of asphalt breaks is called the ductility of the asphalt.

### Melting-point

**Apparatus.**—Outer vessel or container for the glycerin bath, a 600 c.c. Jena beaker, Griffin type.

Inner vessel or air-bath 200 c.c. is a lipless Jena beaker.

Chair or support for inner vessel is cut out of  $\frac{1}{16}$ -in. sheet aluminium.

Cover for inner vessel is cut out of sheet aluminium or brass.

Support for moulds consists of discs of brass with holes tapped for two or four moulds suspended on three hangers.

Commercial glycerin, standard thermometer.

Double thickness 20 mesh iron gauze.

Iron tripod, stand and clamps.

Bunsen or alcohol burner.

FIG. 11.—N. Y. testing laboratory extractor complete.

**Manipulation.**—One or more of the brass moulds standing upon a piece of amalgamated brass or tin should be filled with the bitumen under examination. The bitumen may be softened by cautiously heating it in a small casserole or tin box until it is sufficiently fluid to be poured into the mould. After trimming off the upper surface level with the mould, place the sample in water at 77° F. for about 10 minutes. It should then be suspended in the air-bath of the apparatus and the cover and thermometer placed in their proper positions. The temperature of the glycerin bath should also be 77° F. at the beginning of the test.

The apparatus should stand on a double 20-mesh iron gauze, supported on an iron tripod and heated at the rate of 5° F. per minute. The temperature at which the sample of bitumen flows from the mould and first touches the bottom of the inner vessel, is recorded as the melting or flowing point.

<sup>1</sup> Moulds for bitumen and brass collars used in N. Y. T. L. float test apparatus are made by Howard & Morse, Brooklyn, N. Y.

**Float Test.**—The sample is melted at as low a temperature as possible and then poured into a small brass mould (the same as used in melting point determinations). It is then allowed to cool, placed in water at  $41^{\circ}$  F. for 10 minutes, the edges then trimmed with a hot knife and cooled for 10 minutes longer. It is then screwed into an aluminium float plate or dish about 3 in. diameter and placed in water at  $150^{\circ}$  F. starting a stop watch the moment the float is placed in the hot water. The second the water flows through the melted bitumen into the inside of the float mould is taken as the float.

**Drip Point.**—Melt the sample at as low a temperature as possible and then coat the bulb of a thermometer with the bitumen until a layer  $\frac{1}{8}$  to  $\frac{1}{16}$  in. thick and about 1 in. long is obtained. Cool and place in an air-bath free from currents, which is heated so that the temperature of the air rises about  $2^{\circ}$  C. per minute. The temperature on the thermometer when the first drop falls, is noted as the drip point.

### Fluxes.<sup>1</sup>

By the term "asphalt content" of a flux or road oil, etc., is meant the residue remaining after heating the oil at  $500^{\circ}$  F. until the penetration at  $77^{\circ}$  F. of the residue is 100.

**Sp. gr.** at  $60^{\circ}$  F. or  $77^{\circ}$  F. is determined in a small bottle by weighing in air and water as under Crude Petroleums.

**Flash point** is determined in a New York State Open Cup Tester. This consists in heating the flux in a 3-ounce tin box with a Fahrenheit thermometer inserted so that the temperature of the flux rises  $5^{\circ}$  F. every minute. The point at which the escaping gases catch fire or a lighted taper flashes the entire surface of the oil is noted as the flash point.

**Loss on 20 Grm. at  $212^{\circ}$  F.**—Weigh out 20 gm. into a 3-ounce tin box and note the exact weight. Then put in an oven at  $212^{\circ}$  F. and leave for 5 or 7 hours as specifications call for. Take out from oven, cool and weigh. Calculate loss to per cent.

**Loss on 50 Grm. at  $212^{\circ}$  F.**—Weigh out 50 gm. and follow procedure as above.

**Loss on 20 Grm. at  $325^{\circ}$  F.**—Weigh out 20 gm. in a 3-ounce tin box and put in an electric oven regulated by means of a thermostat at  $325^{\circ}$  F. for 5 or 7 hours as called for. Calculate loss to percentage as above.

**Loss of 50 gm. at  $325^{\circ}$  F.** is estimated in the same way, using 50 gm. instead of 20 gm.

When removing the boxes from the oven it is advisable to tilt them so that on cooling the asphalt is up against one side of the box. This is done when a penetration of the residue at  $77^{\circ}$  F. is required.

**Bitumen soluble in carbon disulphide** is estimated as under *Asphalts* (see Vol. III, p. 77).

<sup>1</sup> Methods of the New York Testing Laboratory.



Mineral matter is estimated as under *Asphalts* (see Vol. III, p. 79).

**Bitumen Soluble in 88° Naphtha.**—Weigh out 1 grm in a 200 c.c. Erlenmeyer flask. Add 100 c.c. naphtha (88° Bé.) and leave over night. Filter through a wide mouth Gooch crucible without suction, wash until the washings are colourless, with 88° naphtha; dry at 212° F. and weigh. If all the asphalt is not washed out of the flask, this is dried and weighed also and the weight of the remaining asphalt added to that on the Gooch. This subtracted from 1 grm. and divided by 100% gives per cent. soluble in 88° naphtha.

### Roofing Papers.<sup>1</sup>

**Method of Testing.**—(1) Make four tests on Mullen (paper) machine. Report average and temperature. (Cut two 3-in. squares, two 6-in. squares, one piece 6×2 in. for subsequent tests.)

(2) Ignite one of the 3-in. squares and calculate per cent. ash.

(3) Extract one 6-in. piece and one 3-in. piece with carbon disulphide in an extractor and calculate per cent. bitumen, etc., as per following formula:

*Formula for calculating bitumen, felt and mineral matter in coating.*

If A = per cent. ash in original sample.

B = per cent. ash in dry felt.

C = per cent. dry felt in original sample.

$A - CB$  = mineral matter in coating.

$100 - C + A - CB$  = bitumen.

(4) Ignite extracted 3-in. square and calculate per cent. ash in dry felt.

(5) Measure thickness of extracted 6-in. square felt.

(6) Make four tests on Mullen machine for strength of dry (extracted) felt. Report average.

(7) Treat 1 grm. of extracted felt with 100 c.c. of 2% sodium hydroxide in a 200 c.c. Erlenmeyer flask with reflux condenser and boil gently for ½ hour.

Filter in a Gooch crucible, washing with hot water, return fibres to flask and treat once more as above. After washing thoroughly with hot water, dry at 212° F. and weigh. Report per cent. dry felt (wool and hair) removed by 2% sodium hydroxide.

(8) Place 2 in.×6-in. strip in ice water at 41° F. and after 15 minutes work over rods ¾ in., ⅝ in., ½ in., ⅜ in., ¼ in., and 180° flat, reporting the diameter of rod over which roofing cracks.

Weight 3-in. square in grams × 16.896 = pounds per 480 sq. ft.

### Estimation of Paraffin in Asphaltum.

Richardson's method of purifying the fraction soluble in light benzin by means of concentrated sulphuric acid (Vol. III, p. 82) is claimed

<sup>1</sup> Methods of the N. Y. Testing Laboratory.

by Marck<sup>1</sup> to be tedious and the use of animal charcoal is recommended by him. 1 grm. of asphaltum is dissolved in 2 c.c. of chloroform, and 50 c.c. of light benzin (b. p. 70° C.) are added. After digesting for 1 hour the liquid is filtered through 40–60 grm. of the dry pulverised charcoal resting on cotton wool moistened with petroleum ether, suction being applied. Washing is effected with three to four portions of 30 c.c. of petroleum ether. The bulk of the solvent is distilled off, the remainder expelled in the oven, and paraffin determined in the residue by the method of Engler-Böhm-Holde (solution in ether and precipitation with absolute alcohol at –20° C.).

**Separation of Natural and Petroleum Asphalt.**—Marcusson has previously recommended the estimation of the oil content as a means of distinguishing between natural and petroleum asphalt, since natural asphalt contains 2–34% oil, practically free from paraffin, while petroleum asphalt contains 26–58% oil, very rich in paraffin. H. Loebell<sup>2</sup> has objected that this method is impracticable in the case of paving asphalts where small amounts of petroleum asphalt are added to Trinidad asphalt as a flux and serve to increase the percentage of oily constituents. Marcusson<sup>3</sup> replies that this fact in itself would be sufficient to show the presence of petroleum asphalt in the natural product and cites numerous examples in support of this contention. Loebell recommends the determination of the paraffin content of the oily portion of the asphalt as a method of distinguishing between natural and petroleum asphalts, the oil from the latter being high in paraffin, but Marcusson points out that certain Roumanian petroleums show a very low paraffin content. The distillation of the asphalts, however, and determination of the acid number of the distillates are of considerable value. Distillates from petroleum asphalts have low acid numbers and free paraffin frequently separates. Natural asphalt distillates have higher acid numbers and show no free paraffin. Determination of the saponification number of the asphalt is also valuable, since this number of natural asphalts runs much higher than that of the petroleum asphalts, 28.5–34 for the former as against 7.6–13.5 for the latter. Of the petroleum asphalts the Californian and Roumanian products have the highest saponification number. Determination of the sulphur content of asphalts is of little value since the sulphur content of certain petroleum asphalts is as high as or higher than that of some natural asphalts.

**The Estimation of Natural Asphalt in the Presence of Artificial Asphalt.**—Marcusson's method<sup>4</sup> is based on the precipitation of sulphonated bitumens from water solution. 10 grm. of material are shaken with 75 c.c. of an ether solution of hydrochloric acid (prepared by shaking ether with conc. hydrochloric acid, keeping the mixture cold) in three or four portions. After 10 minutes 75 c.c. of water are added and the mixture heated on the steam-bath until no more odour of ether is noticeable. The insoluble matter is filtered

<sup>1</sup> *Zeit. anal. Chem.*, 1913, 52, 553–556.

<sup>2</sup> *Chem. Zeit.*, 36, 22–23.

<sup>3</sup> *Chem. Zeit.*, 36, 801–803.

<sup>4</sup> *Z. angew. Chem.*, 26, 91–93.

off, dried and extracted with boiling chloroform; the extract is weighed after distilling off the chloroform and drying at  $105^{\circ}$ . 3 grm. of this bitumen are then treated with 6 c.c. of conc. sulphuric acid and heated on the steam-bath for 45 minutes. The product is treated with 200 c.c. of water. A precipitate settles out which after 1 hour is filtered off, washed free from acid, dried and weighed. This product is the natural asphalt bitumen. The amount of mineral matter in natural asphalt varies enormously, but the valuation of the material is based on its bitumen content. The results are about 4% low. Adding a correction of 4% to results obtained with Trinidad asphalt and coal-tar pitch mixtures, of known composition gave figures fairly close to the theoretical. Petroleum residues react like natural asphalts with sulphuric acid, so that it is necessary to examine the insoluble precipitate for the paraffin content of the oily portion and the acid content of the distillate.

**Estimation of the Asphalt Content of Mineral Oils, Petroleum Pitch and Similar Materials.**—A series of experiments by Schwarz<sup>1</sup> using butanone instead of acetone as prescribed in the official German methods are here given. Butanone is a good solvent for mineral oil distillates and is used in somewhat the same manner for their separation as acetone; the ready solubility of light mineral oils in butanone renders it advantageous in separating asphalt from dark mineral oils. On treating asphaltic mineral oils at room temperature with the solvent, large amounts of light oil are dissolved, whilst black, very viscous to soft pitchy masses, according to the nature of the material, remain undissolved; a sharp separation of the asphalt from the oil could not be obtained by this treatment, but on heating the butanone to boiling ( $81^{\circ}$ ), clear dark solutions were obtained. Butanone has the power of absorbing a significant amount of water, causing a lowering of solvent power and a more perfect separation of asphaltic substances. 1,000 c.c. of butanone at room temperature requires about 110 c.c. of water for saturation; at  $20^{\circ}$  the water-free material has sp. gr. = 0.805, saturated with water = 0.835. Tests were made on cylinder oils using a butanone-water mixture of sp. gr. 0.835 and of 0.812, the latter dissolving all oils and giving a clean, sharp separation from asphaltic matter. Estimations were made for comparison by using alcohol-ether and normal benzine. Results by the butanone and the alcohol-ether methods with some samples agreed very well, but with others there was a variation due to the nature of the asphaltic matter, soft asphaltic substances being dissolved in greater amount by the latter and hard substances less by the former. With normal benzin, the results showed that with increasing content of butanone-insoluble asphalt, there was increase in the precipitate by benzin, with a darker colouring of the benzin solution; larger amounts of asphalt are precipitated with butanone than with benzin. Experiments were made on solid bitumens (Trinidad asphalt, soft Italian asphalt, Galician). Butanone is superior to the usual

<sup>1</sup> *Chem. Zeit.*, 35, 1417.

solvents for separating asphaltene from petrolene in that no chemical change is liable to take place in the constituents from overheating, and because the solvent power may be varied by varying additions of water; this makes it possible to separate the asphalt into a series of characteristic constituents. An accurate study of the latter should contribute to the knowledge of the chemical nature of asphalts and the rôle of sulphur in their formation and properties. Water-free butanone is recommended as a substitute for alcohol-ether in the determination in oils; a single precipitation (cooling of the butanone solution in ice-salt mixture and filtration at 15°) separates total paraffin.

### Mineral Oils.

**Determination of Sp. Gr. of Small Quantities of Mineral and other Oils.**<sup>1</sup>—When the quantity is less than 1 c.c. a sp. gr. bottle of 5 c.c. capacity is filled with about 4.5 c.c. of water and weighed. The oil is poured into the bottle on top of the water and the bottle again weighed. Taking  $d$  as the sp. gr. of the oil under test,  $n$  its volume and  $f$  its weight, we have:  $d = n/f$ . But  $n$  is equal to  $w$  (wt. of water fully filling the bottle) less  $e$  (weight of water and oil) less  $p_1$  (weight of bottle partially filled with water). Thus:  $d = (w - e) / (p_2 - p_1)$ .

**Method of Determining the Sp. Gr. of Heavy Petroleums** (Heavy Crude Petroleums, Viscous Lubricants, "Black Oils," etc.).—J. McC. Sanders<sup>2</sup> describes the following method: The apparatus consists of two 100 c.c. burettes, a 100 c.c. cylinder, a thermometer, rubber-tipped glass rod, and a glass tube curved at one end in a semicircle, and having a small rubber bulb fastened on the other. Two mixtures of pure alcohol and water are required, one containing 50% and the other 75% alcohol by volume. The burettes are supported on opposite sides of the cylinder. Into the cylinder about 75 c.c. of the dilute mixture are run from one of the burettes. The oil is poured into the glass tube and the tube is then immersed in the liquid and a small drop of oil is forced out by means of the rubber bulb. If the sp. gr. of the oil is less than that of the mixture of alcohol and water, the drop will rise to the surface and can be removed by touching it with the rubber-tipped rod. In this case a portion of the stronger alcohol is run in from the other burette, well mixed, and another drop of oil forced out. These operations are repeated until the sp. gr. of the mixture and the oil drops are identical. The volume of the two alcohol solutions used to form the mixture are read off from the burettes, and the sp. gr. of the mixture is calculated from the amounts used.

**Sulphur** (According to Richardson, Private Communication).—About 0.2–0.3 grm. oil (or asphalt) is weighed out on a small cylindrical absorp-

<sup>1</sup> *Petroleum Rev.*, 28, 252.

<sup>2</sup> *Proc. Chem. Soc.*, 27, 250.

tion disc and is burned in an atmosphere of oxygen in a large glass bottle. The oil is kindled by an electric spark which burns a piece of iron wire and the fire is communicated to the disc by a thread of cotton. As soon as the combustion is complete, the bottle is cooled so as to form a vacuum. A solution of sodium dioxide is then drawn in through a separating funnel, and the bottle is shaken so that all sulphur dioxide is absorbed and oxidised by the alkali. The alkali is then poured into a beaker, the bottle rinsed two or three times and the rinsings added to the alkaline solution. This is then boiled, filtered, acidified with hydrochloric acid, taking care to cover the beaker with a watch glass to prevent loss by effervescing. After all the hydrogen dioxide has been boiled out, the solution is neutralised with ammonia, then slightly acidified with hydrochloric acid and the sulphur trioxide precipitated with barium chloride in boiling solution. The mixture is boiled 5 minutes and left overnight. The barium sulphate is collected on a Gooch crucible, dried, ignited and weighed.

**Estimation of Sulphur in Petroleum Illuminating and Lubricating Oils.—**

A large proportion of the total sulphur in many inferior, poorly refined petroleum oils is present as sulphonates or sulphates; these compounds are not included when the sulphur is estimated by ordinary "lamp" methods, since they remain in the wick, and although included when direct oxidation methods are employed, no distinction is made between them and the sulphur compounds normally present in the oil. The method employed by Conradson<sup>1</sup> consists in burning to dryness a weighed quantity of the oil by means of an ordinary kerosene burner and aspirating the products of combustion through two absorption tubes arranged in series and containing a solution of sodium carbonate (6 grm. per litre) previously standardised with *N/10* acid. 10–20 grm. of illuminating or 5–10 grm. of lubricating oils are usually taken for the determination; the more viscous oils are mixed with an equal volume of highly refined kerosene of known sulphur content, and when the mixture has burned completely, a further 2 c.c. of the kerosene are added and burned to dryness. The sodium carbonate solution (including the rinsings of the apparatus) is either titrated with standard acid or oxidised with bromine and hydrochloric acid and precipitated with barium chloride as usual. The examination of the wick for sulphur compounds is conducted as follows: When only the total sulphur (sulphonates and sulphates) is required, the wick, cut into small pieces, is digested with 0.2 grm. of sodium carbonate and 5 c.c. of concentrated nitric acid until the fibres are disintegrated, when 2 grm. of magnesium nitrate are added and the temperature is gradually raised until the organic matter is destroyed; the sulphur contained in the residue is then estimated by the usual means. When separate estimations are required of the sulphur present as sulphonates and sulphates, the wick is boiled with a solution of barium hydroxide which

<sup>1</sup> 8th Int. Cong. Appl. Chem., 1912; Sec. I, Orig. Comm., I, 133–136.

is then diluted and filtered. The filtrate, containing the sulphonates, is either oxidised with bromine and hydrochloric acid, or evaporated to dryness with nitric acid (the residue being treated with hydrochloric acid and boiling water), to effect the precipitation of the barium sulphate representing the sulphonates originally present. The sulphur in the residue from the barium hydroxide treatment is estimated by the method employed in estimating the total sulphur in the wick (see *Sulphur Method*, pages 247, 248).

**Water in Crude Petroleum.**—Weigh out 100 grm. of the thoroughly mixed sample into a 500 c.c. distilling flask. Add 100 c.c. of heavy benzin (62° Bé.) and connect the flask to a water-jacketed condenser. Distil until no more water passes over, which can easily be observed by an absence of bumping. Collect the distillate in a 100 c.c. graduated cylinder, the first 10 c.c. of which are graduated in tenths of a c.c. Rinse out the condenser with naphtha and then read the volume of water which settles to the bottom of the cylinder. This reads directly as a percentage.

**Method of Drying Oil.**—(1) The crude oil is dried either by warming with calcium chloride in a flask with an inverted glass condenser, and then filtering through cheese-cloth.

(2) By distilling the oil in a copper still until all water has passed over. The distillate which consists of water and light oils is collected in a separating funnel, the lower layer of water drawn off and the light oily layer is added to the residue in the still as the dried sample.

Both of these methods are at fault, however, in that there is a slight loss of the lighter oils, a difficulty that is very hard to overcome.

**Analysis of Heavy Naphtha and Distillates.**—Sp. gr. at 60° F. is best determined by the Westphal balance. *Flash and Fire Tests.* Determine with Tagliabue Cup.

**Loss on Spontaneous Evaporation.**—Weigh 10 c.c. of the oil from a pipette into a 3½ in. crystallising dish and allow to stand 24 hours at a temperature of 77° F. (25° C.) Weigh again and calculate loss as percentage.

**Sulphuric Acid Absorption.**—Into a 20 or 30 c.c. carbon tube measure exactly 10 c.c. of the oil and 10 c.c. of conc. sulphuric acid. Mix thoroughly and allow to stand about 30 minutes. Note the amount of oil absorbed by the acid and report as percentage.

**Colour** is obtained by matching the oil in a 1-in. (or fraction thereof) cell with standard tints, in a Lovibond Tintometer.

**Estimation of Hard Asphalt in Mineral Oils by Normal Benzin.**—According to L. Allen's Laboratory, Hamburg.<sup>1</sup> A cylinder oil containing 0.2% hard asphalt was treated according to Holde's directions with normal benzin, but the residue did not look like asphalt and was soluble in absolute alcohol, leaving only 0.018% asphalt. A similar removal of paraffin compounds by absolute alcohol from "hard asphalt" residues was observed by Ubbelohde.

<sup>1</sup> *Chem. Rev. Fett-Harz-Ind.*, 20, 192.



**Oxygen in Bitumens.**—A process has been described by S. P. Sadtler<sup>1</sup> which is a development of that of W. M. Cross, and is carried out as follows: A fused silica combustion-tube 30 in. long is partly filled with iron wool and placed in a combustion furnace. In one end of the tube is a boat containing the weighed sample of asphalt. The other end is connected in succession with a U-tube filled with spun glass, and a weighed calcium chloride tube. The part of the tube filled with the iron wool is strongly heated while that in the vicinity of the boat is kept cool by trickling water over it. Hydrogen is passed slowly through the apparatus until the calcium chloride tube has attained a constant weight. The boat is then gradually heated until ultimately it and its contents attain the maximum temperature possible, which is so maintained for a time. The water formed will be completely carried into the calcium chloride tube if the hydrogen is passed through long enough. Any sulphur present will unite with the heated iron wool. The hydrogen used is dried and purified by passing it slowly through concentrated sulphuric acid, over calcium chloride and then over phosphorus pentoxide.

**Carbon Test and Ash Residue in Petroleum Lubricating Oils.**—Conradson's apparatus<sup>2</sup> consists of an iron crucible or retort having a diameter at top of 80 mm., bottom 45 mm., height 55 mm. Inside the crucible is placed, upon a support, either a glass crystallising dish (65 mm. in diam.) or a 70–80 c.c. platinum dish; the latter is preferred for further study of the carbon residue. In the lid of the retort are attached two tubes, (1) an exit or delivery pipe 7–8 mm. in diameter, bent and attached to a condenser, and (2) a tube 2 mm. in diameter, for blowing out the heavy fumes. 35 gm. of the oil are placed in the weighed dish, the cover clamped down, using an asbestos washer, and the apparatus put on an asbestos block resting on a tripod and covered with a sheet iron or asbestos hood on top of which is a clay chimney, to distribute the heat uniformly. To get the upper part of the apparatus hot at the beginning, a large gas flame is used at the start for a few minutes, when it is subsequently lowered; the distillation should be uniform and at the rate of 1 c.c. per minute. At the end of the distillation, the flame is raised gradually to make the bottom and lower part of the apparatus red hot, when heavy fire test oils are tested, and through the inlet pipe attached to a rubber tubing carbon dioxide or another suitable gas is momentarily blown to expel the heavy, dense fumes or vapours. After cooling, the dish containing the carbon residue is weighed, the latter ground fine and leached out with boiling water (the solution is tested with litmus paper and with silver nitrate for chlorine); next digested with hot hydrochloric acid (1:1), filtered, washed, dried, and weighed. The difference in weight gives approximately the amount of foreign matter in the carbon residue. The carbon residue transferred back to the platinum dish is burned off, adding a little ammonium nitrate; if any residue is left it is weighed and deducted from the last carbon weight and

<sup>1</sup> *Orig. Com., 8th Intern. Congress Appl. Chem. (Appendix), 25, 729–733.*

<sup>2</sup> *Orig. Com., 8th Intern. Congr. Appl. Chem., I, 131–132.*



dissolved in hydrochloric acid. The water and hydrochloric acid solutions are united and examined for impurities (*e.g.*, Fe, Al, CaO, MgO, Na<sub>2</sub>O, SO<sub>3</sub>). Some lubricating oils contain oleates of lead, aluminium, zinc, calcium or magnesium held either in solution, or suspension or both; before making the above test it should be ascertained if any of these compounds are present.

### Proposed Provisional Tests for Lubricants.<sup>1</sup>

**Viscosity**<sup>2</sup> shall be determined with the Saybolt universal viscosimeter, the dimensions of which are as follows:

Diameter of overflow filling gauge cup.....	51.0 mm.
Depth of overflow filling gauge cup.....	13.0 mm.
Diameter of main cylindrical tube.....	30.0 mm.
Depth from starting head to outlet jet.....	113.0 mm.
Length of outlet jet.....	13.0 mm.
Diameter of outlet jet.....	1.8 mm.
Charging quantity.....	70.0 c.c.

Tables for the conversion of the readings of other instruments into those of the Saybolt universal viscosimeter are now in preparation by the U. S. Bureau of Standards.

**Sp. Gr.**—For all practical purposes there is little to choose between the hydrometer, Westphal balance or Geissler pycnometer, provided these instruments are verified. The observations should be taken with the oil at 15.56° (60° F.) and compared with water at the same temperature.

For Baumé hydrometers the committee recommends the use of those based on the formula of the Bureau of Standards:

$$\text{Sp. gr.} = \frac{140}{130 + \text{Bé. } 60^{\circ}/60^{\circ} \text{ F.}}$$

It should be understood, however, that many Baumé hydrometers now in use are not based on this formula and in converting the readings of any Baumé hydrometer to sp. gr. care should be taken to use the formula on which the instrument in question is based.

**Flash and Fire Test.**—With the *Cleveland Open Cup*.—The cup is filled to about 1/4 in. from the top and the thermometer is suspended so that the bulb is just immersed in the oil. The oil is heated at the rate of 10° F. per minute by a Bunsen burner with a protecting chimney; as the flash point is approached a test is made for every rise of 3° F. by slowly passing the small bead-like test flame across the cup near the thermometer. The oil should flash near the thermometer when the proper point is reached. The fire test is, as a rule, 50 to 80° F. higher than the flash point. As the open-cup tests are easily affected by draughts they are subject to errors of 5° F. If the thermometer is graduated to read for total immersion, the stem correction should be applied. When this is done it is suggested that “corr.” be added to the reading, thus, “flash 379° F. corr.”

<sup>1</sup> *Proceedings of the Amer. Soc. for Testing Materials*, 1914, 14, Part I, 358.

<sup>2</sup> The minority report recommended that the Engler method be an alternative method.

**Pensky-Martens Test.**—Where greater accuracy is required the Pensky-Martens tester should be employed. The method of operating is as follows:

The oil container is placed in a metal heating vessel provided with a mantle in order to protect the heating vessel from loss of heat by radiation. The oil cup is closed by a tightly fitting lid. Through the centre of the lid passes a shaft carrying the stirring arrangement, which is worked by means of a handle. In another opening of the cover a thermometer is fixed. The lid is perforated with several orifices, which are left open or covered, as the case may be, by a sliding cover. This can be rotated by turning the vertical spindle by means of the milled head. By turning this head an opening of the slide can be made to coincide with an orifice in the cover, and simultaneously a very small flame, burning at the movable jet is tilted on to the surface of the oil.

The test is performed by filling the oil into the oil cup up to a certain mark, fixing the cover and heating the oil somewhat rapidly at first, until its temperature is about  $30^{\circ}$  below the expected flash point. The temperature is then allowed to rise only very slowly, by making suitable use of the wire gauze so that the rise of temperature within a half minute does not exceed about  $2^{\circ}$ . Every  $1.05^{\circ}$  the milled head is turned and the flame tilted into the oil cup. The temperature at which a slight explosion is produced is noted as the flash point of the oil.

**Soap Test.**—The test depends upon the fact that the metaphosphates of the earthy and alkali metals and aluminium are insoluble in absolute alcohol. 5 to 10 c.c. of the oil are dissolved in 5 c.c. of  $86^{\circ}$  benzin, and 15 drops of a saturated solution of "stick phosphoric acid" in absolute alcohol are added, shaken and allowed to stand; the formation of a flocculent precipitate indicates the presence of soap. For the accurate determination of these soaps a known quantity of the oil must be ignited and the residue quantitatively examined.

**Saponification Value.**—This is expressed by the number of milligrams of potassium hydroxide necessary to saponify 1 grm. of the oil. From 2.5 to 10 grm. of the oil, according as 65 to 20% of saponifiable matter are supposed to be present, are boiled with 25 c.c.  $N/2$  alcoholic potassium hydroxide in a 200 c.c. Jena Erlenmeyer flask. A reflux condenser is used and the boiling may require from 5 to 8 hours. The excess of alkali is titrated with  $N/2$  hydrochloric acid, using phenolphthaleïn. The strength of the  $N/2$  potassium hydroxide is determined by boiling 25 c.c. in a similar flask alongside of those in which the oil is treated and for the same length of time.

Alcohol purified with silver oxide according to Dunlap's method should be used, as well as potassium hydroxide "purified by alcohol." For heavy oils, dissolve them in sufficient chemically pure benzol to make a clear solution before adding the potassium hydroxide. Usually 50 c.c. will suffice.

**Free Acid.**—About 10 grm. of oil are weighed into a 200 c.c. Jena Erlenmeyer flask; 60 ~~c.c.~~ of neutral alcohol added, the mixture warmed to about 60° C. and titrated with *N*/6 potassium hydroxide, using phenolphthaleïn, the flask being frequently and thoroughly shaken.

The free acid, if present, should be reported as the number of milligrams of potassium hydroxide necessary to neutralise the acidity in 1 grm. of oil, and the nature of the acid stated if possible.

**Sulphur Test.**—Proceed as follows: A portion of a sample, 0.7 to 1.0 grm. is burned in a calorimetric bomb containing 10 c.c. of water and oxygen under a pressure of 30 atmospheres. A lower pressure sometimes gives inaccurate results. If the sample contains more than 3% of sulphur the bomb is allowed to stand in its water-bath for 15 minutes after ignition of the charge. In case the sulphur content is as high as 5%, oxygen under pressure of 40 atmospheres is used. With these high pressures in a Berthelot bomb of 500 to 600 c.c. capacity, repeated trials have failed to show even traces of carbon monoxide or sulphur dioxide. If a smaller bomb of about 175 c.c. capacity, such as the Peters or Kroeker, is used, incomplete combustion from a lack of oxygen may result if too large a sample is taken.

After cooling—15 minutes is usually enough—the bomb is opened and its contents are washed into a beaker. If the bomb has a lead washer, 5 c.c. of a saturated solution of sodium carbonate are added, the contents are heated to the boiling point, boiled for 10 minutes and then filtered. This operation is necessary to decompose any lead sulphate from the washer. The united washings are then filtered, acidified with hydrochloric acid, boiled to expel all carbonic acid and the sulphuric acid-content is determined in the usual way with barium chloride.

Gravimetric determination is preferred to volumetric, because the nitrogen contained in the air originally in the bomb is oxidised in part to nitroacids, which cause a small error if the volumetric determination alone is used. The sulphur content of any combustible material, from light gasolines weighed in a tared gelatin capsule to solid bitumens and cokes, can be readily determined by this method.

This method of burning in a bomb is accurate, practicable and rapid, and is recommended in preference to all of the other methods described. The calorimetric determination, if desired, can be made at the same time (see page 247 for sulphur in asphalt and bitumens).

**Test for Water.**—Dilute the oil with an equal volume of benzene which has been previously saturated with water. Warm to 32°. Whirl vigorously in a centrifuge until the separated layer of water does not appear to increase in volume.

**Alternative Method.**—The water content may be determined as follows: 80 grm. of the sample are weighed into a 250 c.c. distilling flask and an equal quantity of xylol or benzin, having an initial boiling point of about

150°, is added. The distillation is carried out at the ordinary rate of 1 drop of distillate per second until 163° is reached. In the event of a few drops of water adhering to the condenser and failing to run into the receiver, they may be removed with a weighed pellet of cotton and the amount of water so obtained added to that found in the distillate.

**Precipitation Test.**—Dissolve 10 c.c. of oil in 90 c.c. of 86 to 88° benzin (from Pennsylvania crude) in a tapered graduated tube. Whirl in centrifuge until no further change in the amount of precipitate is observed.

**Microscopical Examination.**—Put a few drops of the well-mixed oil on a slide and note the nature of the suspended matter—whether carbonaceous specks, flakes of paraffin which disappear on warming, or foreign matter. Polarised light is a great aid in detecting paraffin crystals, showing them white

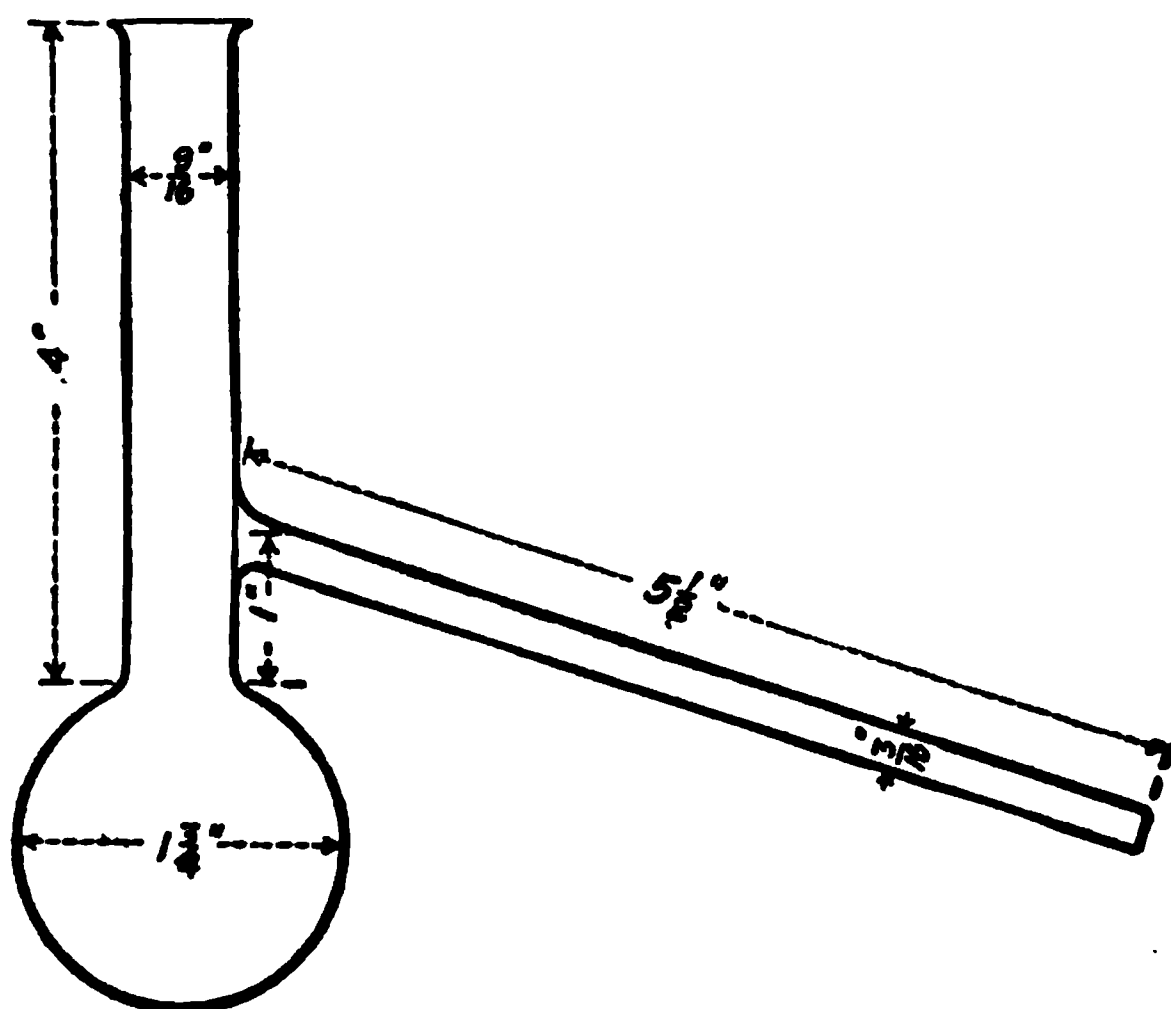


Fig. 12.—“Gray” Carbon Residue Flask.

on a black background. The polariscope is excellent for this same purpose, showing them when it is impossible to see them with direct light.

**Carbon Residue Test (T. T. Gray's Method).**—To a tared 1-ounce flask of the dimensions shown in Fig. 12 preferably of quartz, add 25 c.c. of the oil to be tested and weigh. Wrap the neck of the flask with asbestos paper as far down as the side arm. Stopper tightly with a good cork. Connect to a small aerial condenser by plugging the space with asbestos or glass wool. Provide a shield which will protect the flame and the flask up to the side tube. Using the flame of a good Bunsen burner, heat the flask so that the first drop of distillate will come over in approximately 5 minutes. Continue the distillation at such a rate that 1 drop per second will fall from the end of the condenser. As the end of the distillation approaches, increase the heat just enough so that the heavy vapors are allowed to con-

dense and drop back into the flask; continue increasing the heat until the flask is enveloped in the flame, and maintain the temperature 5 minutes. Allow the flask to cool, remove the asbestos covering and cork, and burn out completely the carbon and oil in the neck as far down as the side tube and in the side tube. Heat the bottom of the flask until no more vapours are given off, cool and weigh.

**The viscosity of lubricating oils** is measured by the Ostwald viscosimeter described in text-books of Physical Chemistry (*e.g.*, Findlay's Practical Physical Chemistry).

Filtered oil is run into the viscosimeter to the marks *c-d*. It is now suspended in a bath of paraffin wax or suitable clear high flash oil. It is adjusted quite vertically by reference to plumb lines suspended in the bath. A 2-litre Jena beaker forms a convenient bath, and stirring may be carried out by means of a glass paddle, run by a hot-air motor. A delicate thermometer is immersed in the bath. If the determinations are carried out in a suitable place, well shielded from draughts of air, steady temperatures may be maintained for long intervals. It is advisable, however, to guard the apparatus with asbestos millboard as a protection against temperature fluctuations. After the viscosimeter has been immersed 15 minutes at constant temperature, the levels of the oil should be accurately adjusted to the marks *c-d*, by means of a warmed glass pipette. Rubber tubing is fixed to the top of bulb *A*, and the oil slowly sucked up above mark *a*. It is then allowed to flow down and when the meniscus passes *a*, a stop-watch reading to fifth seconds is started and the time of flow between *a* and *b* is taken. Four or five determinations are made and averaged. For ordinary oils the following dimensions will be found useful: Capillary, *C*, 6 cm.  $\times$  1 mm. bore; bulb *A*, 4 c.c.; bulb *B*, 8 c.c.; length over all 15 cm. The viscosimeters may be obtained from Messrs. Müller, Orme, & Co., High Holborn, England.

**Specifications for Gas Oils for Railways.**—The most important characteristic of the oil is its "heat yield" (the product of the yield of gas and the heating value of the gas). This is nearly independent of the temperature of gasification. It varies with the hydrogen content of the oil; but the loss on compression of the gas depends on the hydrogen content of the oil. Since for railway purposes the gas is always compressed, it is the "heat yield" of the gas after compression which is of interest. Where the gas is to be used in open flame burners, the "light yield" (candle power yield) is of more importance, but this is commonly not the case in railway lighting. Of impurities in the oil, sulphur, water, and creosote are to be controlled; nitrogen and oxygen are of no importance. In sampling deliveries, representative samples for water are exceedingly difficult to obtain. By gently heating a sample of the oil it is freed from water, the sp. gr. of this taken, the volume of oil de-

<sup>1</sup>Landsberg, *J. Gasbel.*, 56, 10-14.

livered (as shown by measurement or a meter), multiplied by this sp. gr. and the resulting weight subtracted from the shipper's weight is taken to give the water. For determining the "heat yield," a 1-hour actual run, requiring 300–450 kg. oil, is sufficient.

**Transformer Oils.**<sup>1</sup>—A good transformer oil must have a large insulation capacity. It must be absolutely free from water, be neutral, and to be safe must have high flash and solidifying points. The bath in which the insulation capacity is determined is made of glass, insulated from the earth by porcelain strips resting upon a glass plate; the electrodes are of brass, fitted with porcelain clasps at the point through which they pass the hard gum cover of the bath. Three freshly refined oils with viscosities ranging from 3.8° to 20° (Engler) at 20° were examined. With the electrodes 5 mm. apart, and voltage of 10,000, no spark passed after 20 minutes. When the voltage was increased gradually to 40,000 a spark passed through the heaviest oil after 5 seconds, through a lighter oil after 30 seconds, and through the lightest oil after 60 seconds. The insulation capacity increases with viscosity. The oil loses its insulation power with usage. An oil with a viscosity of 8° (Engler) at 20°, which had been in use for 3 years, allowed no passage of a spark at 10,000 volts, but did so immediately at 17,000. When first tested this oil allowed no passage at 18,000 volts after 5 minutes. The changes in temperature cause the oil to darken and a black sediment is deposited. This powder (sp. gr. about 1) is soluble in benzene, ether, carbon disulphide and concentrated sulphuric acid, but is insoluble in benzin, alcohol, and lubricating oil; it does not melt, it cokes on heating, and corresponds to a highly oxidised asphalt. The formation of this resinous matter is undesirable on account of the possibility of a short circuit. The asphaltic content of a transformer oil is determined by passing oxygen through the oil heated to 120° for 70 hours, dissolving the oil in benzin, and filtering the insoluble matter on a weighed filter. The formation of this resinous matter depends chiefly upon the degree of refining, and upon the viscosity of the oil. An oil with a viscosity of 6° Engler at 50°, unrefined, gave after heating for 70 hours, and passing oxygen through the oil, 1.09% of resinous matter; when refined with 10% of sulphuric acid only 0.036% of insoluble matter was obtained, and, when refined with 10% sulphuric acid and decolourised with 4% of sodium silicate, but 0.019% was obtained. The conclusion is reached that a light spindle oil with a viscosity of 3° to 5° at 20°, and 150°–160° flash point is the most desirable for a transformer oil. The disadvantage of the greater evaporation must be weighed against the advantages of a large insulation capacity, but slight decomposition, and cheapness.

**Evaporation Test for Mineral Lubricating and Transformer Oils** (U. S. Bureau of Standards).—In order to obtain comparative results in the evaporation test of mineral oils, the same weight of oil must always be heated in vessels

<sup>1</sup> P. Breth, *Petroleum*, 7, 290–291.



of the same size, so that the oil surface shall always be the same in area and the convection effects be alike. Brass vessels are preferable to those of glass, because they can be made with their walls and bottoms of the same thickness, thus insuring more uniform heating. A convenient size is 5 cm. in internal diameter with sides 3 cm. high. Tubing of this size with a wall thickness of 0.75 mm. can be bought. The bottoms may be made of sheet brass not more than 0.5 mm. thick. It is best to use silver solder, so that the heating need not be limited to the lower temperatures. A vessel of the size indicated weighs somewhat less than 42 gm.

A convenient weight of oil is 5.0 gm. To avoid smearing oil on the walls of the tubes the writer used a small pipette with a 2 cm. stem below the bulb. The final adjustment of the weight was made by just touching an oily or a dry stirring rod to the surface of the oil. It is comparatively easy to weigh out the oil within 0.5 mg. of the amount desired, though a much larger variation would be of little consequence in calculating the percentage of evaporation.

In a neutral atmosphere there might have been somewhat greater losses, and possibly still greater differences between the losses with increasing diameter of tube, than the amounts found. In the air there is more or less oxidation, partly involving loss of carbon dioxide and water, but mainly due to the formation of compounds containing carbon, hydrogen and oxygen, which are precipitated in part from the oil as a fine, brown sediment. The observed losses are really the sum of volatile oil, carbon dioxide and water lost, minus the oxygen taken up.

It would be interesting to repeat the work herein described using an atmosphere of carbon dioxide, nitrogen or steam instead of air, but the results would be of less general application.

**Estimation of Paraffin in Mineral Oils** (According to Schwarz and von Huber).<sup>1</sup>—1–5 gm. of distillate (less for paraffin pulp) are dissolved in 20 c.c. of 0.812 butanone in a test-tube of 25 mm. diameter at room temperature. After cooling to  $-20^{\circ}$  more butanone is added to keep all oil just dissolved. The precipitate is dissolved in benzin, evaporated and weighed. The washing is effected with four to five portions of 5–10 c.c. of 0.812 butanone. Comparison with the Engler-Holde method shows good agreement, the latter showing sometimes low results by 1% when high in paraffin on account of its solubility in the alcohol-ether mixture used in the Engler-Holde method.

**Analysis of Mixtures of Ceresin and Paraffin.**—Since ceresin, made by chemical treatment from Galician ozokerite, costs about six times as much as distilled paraffin, methods of separation have been worked out by N. Chercheffsky<sup>2</sup> to be applied to the unsaponified residue obtained in the ordinary way in fat analysis. It was assumed that the melting point of commercial ceresin is fairly constant about  $69^{\circ}$ , and that the most likely adulterant is

<sup>1</sup> *Chem. Rev. Fett-Harz-Ind.*, 20, 242–244.

<sup>2</sup> *Mal. grasses*, 4, 2235–2239; *Seifensieder Ztg.*, 38, 986–987.



paraffin of melting point about  $52^{\circ}$ . (1) Solubility in carbon disulphide (paraffin, 19.07 grm.; ceresin, 1.97 grm. per 100 c.c. at  $15^{\circ}$ ) and in carbon tetrachloride (paraffin, 11.78; ceresin, 1.95). (2) Critical solution temperature: this is said to be almost independent of the proportion of solvent and substance used; it is the temperature, at which a mixture, heated in a sealed tube until the meniscus of separation becomes horizontal, becomes turbid on being shaken and allowed to cool. Alcohol of 96.5% is recommended as solvent; in this case ceresin becomes turbid at  $172.5^{\circ}$  and paraffin at  $148^{\circ}$ . Various known mixtures of ceresin and paraffin gave results within  $0.6^{\circ}$  of calculated temperatures. (3) Temperature of turbidity, method of determination same as last, except that the tube is open. In case of benzene which is recommended as solvent for this test, the temperature is  $47.4^{\circ}$  for pure ceresin, and  $24.7^{\circ}$  for paraffin. (4) The index of refraction of pure ceresin at  $78^{\circ}$  is 1.4352, at  $100^{\circ}$ , 1.4268; of paraffin, 1.4280 and 1.4185 respectively. In all cases, the values obtained with mixtures are approximately arithmetically proportional to the values of the pure constituents.

G. Armani and G. A. Rodano<sup>1</sup> recommend for the detection and approximate determination of ceresin in admixture with paraffin a method based upon the difference in the critical temperatures of solution of the two substances in a mixture of equal volumes of absolute alcohol and benzene. 0.1 grm. of the sample is dissolved in 10 c.c. of the solvent and the hot solution is allowed to cool slowly, the temperature at which a turbidity or separation of the dissolved substance is observed being noted. For pure ceresin the critical temperature is  $50^{\circ}$ , whilst for mixtures of ceresin and paraffin containing the per cent. of ceresin given, the critical temperatures are: 90,  $48^{\circ}$ ; 80,  $47.5^{\circ}$ ; 70,  $47^{\circ}$ ; 60,  $44.5^{\circ}$ ; 50,  $43^{\circ}$ ; 40,  $41.5^{\circ}$ ; 30,  $40^{\circ}$ ; 25,  $38^{\circ}$ ; 20,  $36.5^{\circ}$ ; 10,  $30^{\circ}$ ; and 5% of ceresin,  $27^{\circ}$ . With paraffin alone, the critical temperature of solution is usually about  $25^{\circ}$ , but may vary in different kinds from  $20^{\circ}$  to  $28^{\circ}$ . In all cases examined, however, of mixtures of paraffin with 10% ceresin, the critical temperature was  $30^{\circ}$ . In applying the method to candles, 0.1 grm. of the sample is tested as described above; if the critical temperature is below  $28^{\circ}$ , the presence of an appreciable quantity of ceresin is excluded. If a higher critical temperature is observed, a portion of the sample is subjected to repeated saponification with an aqueous alcoholic solution of potassium hydroxide (40 grm. dissolved in a mixture of 100 c.c. of water and 200 c.c. of alcohol), and 0.1 grm. of the unsaponifiable matter is tested as described above in order to determine approximately the proportion of ceresin present.

**Paraffin.**—Weigh out 50 grm. of the oil into a tared iron retort. The cover of the retort is bolted on to the latter with a gasket of heavy wrapping paper separating the two. The distance from the retort to the receiver must

<sup>1</sup> *Ann. Lab. Chim. Centr. delle Gabelle*, 1912, 6, 109–118.

be at least 30 in., 20 in. of iron tubing and a 10-in. glass tube. Distill so that all distillate passes over in not more than 25 minutes.

Collect the distillate in a 3-ounce tin box. The glass tube is heated in order to remove any adhering distillate into the receiver. Weigh the retort after it has cooled to obtain the weight of the coke. The distillate is warmed in order to dissolve the thick oils and get an average sample. Now weigh out 5 gm. of the distillate into a small Erlenmeyer flask, add 25 c.c. ether and 25 c.c. absolute alcohol and freeze in an ice and salt mixture together with a wash bottle containing alcohol ether (1:1) mixture for 40 minutes. At the same time a funnel is prepared which is also surrounded with the freezing mixture. At the expiration of the required time filter the paraffin on a hardened filter paper using suction, washing out the flask and the paraffin with alcohol ether until free from colour. Remove the paper from the funnel, scrape off the paraffin with a knife into a tared crystallising dish and dry at  $100^{\circ}$  until all alcohol ether is dissipated. Cool and weigh. Calculate per cent. paraffin in the distillate, then in the original oil by subtracting per cent. coke from 100% and multiplying the per cent. paraffin in the distillate by this figure.

**Vaseline Oil for Internal Use.**—According to A. Vicario<sup>1</sup> vaseline oil or liquid paraffin is obtained from petroleum oils poor in vaseline, and is expressed in the process of preparing solid paraffin. As required by the French Codex it should be of Caucasian origin and consist of hydrocarbons of the series  $C_nH_{2n}$ . By comparison of the rate of flow through a fine tube at the ordinary temperature it should have a viscosity 8–19 times greater than that of water. The sp. gr. varies between 0.840 and 0.890. Acids and fatty substances should be absent. American oils which are in some cases less pure and limpid than the Russian oils have a sp. gr. of 0.870–0.945, and give a yellow to a black colouration when shaken with concentrated sulphuric acid till the latter ceases to be coloured. The oily layer is then separated, washed with sodium carbonate solution, dehydrated with anhydrous sodium carbonate and filtered. When subjected to artificial digestion experiments under varying conditions, the oil was unattacked. American oils have been recently improved and these oils should act like Russian oils in the sulphuric acid test.

### Cyclic Hydrocarbons.

**Testing Commercial Benzols.**—Owing to the increasing demand for pure toluene benzol is produced of great purity at a minimum cost. Therefore its analysis is relatively simple. The distillation test in Vol. III, p. 208 is quite satisfactory for the testing of such pure products (see *Methods of Technical Analysis* by Lunge-Keane, 2, p. 784). See also pages 230 and 234.

A reliable method for the assay of commercial benzols, which is in general

<sup>1</sup> *J. Pharm. Chim.*, 1914, 9, 149–154.

use in Germany, is the result of a proposal due to Lunge<sup>1</sup> for the attainment of uniform methods of analysis for benzols. A spherical vessel 66 mm. diam., made of strong copper 0.6 to 0.7 mm. thick, which is slightly flattened at the bottom, is used for the distillation. It has a neck 25 mm. long, the diameter of which is 22 mm. at the top and 20 mm. at the bottom, for the reception of the glass prolongation, which is 150 mm. long and 14 mm. wide. In the middle of the glass portion is a bulb of 30 mm. diameter, above which, at a distance of 10 mm., a side-tube of 8 mm. diameter is sealed almost at right angles. The glass column and the spherical vessel are connected by means of a good cork stopper. A Bunsen burner of about 7 mm. diameter or a benzin spirit lamp is used for heating. The burner is placed in a tinplate cylinder provided with a door, and also with four round holes 10 mm. above the bottom, and four more 10 mm. below the top, for ventilation. This small heater is covered at the top with a sheet of asbestos having a round hole of 50 mm. diameter in which the spherical retort is placed. The inner tube of the glass Liebig condenser has a length of 800 mm., and is inclined with the outlet 100 mm. below the level of the inlet. The thermometer is made of thin glass, and is graduated in  $\frac{1}{10}$ ths of a degree for pure benzene, and in  $\frac{1}{5}$ ths of a degree for commercial products; it should be about one-half the diameter of the neck, and must be so fixed that its bulb is exactly in the middle of the widened part, and should be compared from time to time with a standard thermometer. The distillate leaves the condenser through a bent adapter, and runs down the sides of a 100 c.c. graduated cylinder.

To carry out the valuation, 100 c.c. of the liquid are put into the flask and the distillation is conducted so that 5 c.c. distil over per minute, *i.e.*, 2 drops per second; it is complete when 95 c.c. have distilled over. In order to correct any cause of error due to different barometer readings, the method of Bannow can be employed, in which the thermometer reading is checked by distilling 100 c.c. of water in the same vessel and observing the thermometer reading at the boiling point of the water, when 60 c.c. of the water have distilled over. It is simpler, however, to utilize Lender's corrections as follows:

(1) When the barometer stands at 720 to 780 mm. the percentages of the distillate obtained are reduced to the corresponding amounts for the normal reading of 760 mm. by applying the following corrections:

For 90 % benzol, 0.033 %.  
For 50 % benzol, 0.077 %.

to be added or subtracted for each millimetre of difference.

(2) For barometer readings of from 720 to 780 mm. for distillation up to 100°, for each millimetre difference add or subtract:

For 90 % benzol, 0.0453°.  
For 50 % benzol, 0.0461°.

<sup>1</sup> *Chem. Ind.*, 1884, 1, 50.

(3) In the case of pure products, the difference of temperature for each millimetre difference in the barometer readings between 720 mm. and 780 mm. is:

Benzene, about 0.043°.  
Toluene, about 0.047°.  
Xylene, about 0.052°.

**Example.**—In the case of a 90% benzol, 88.8% distilled over at 100°, the barometer reading being 721.2 mm. to reduce the percentage to the standard reading of 760 mm.:

$$\begin{aligned} 760.0 - 721.2 &= 38.8 \text{ mm.} \\ 38.8 \times 0.033 &= 1.28 \text{ \%} \\ 88.8 - 1.28 &= 87.52 \text{ \%} \end{aligned}$$

at 100°.

Or, if the distillation of the same benzol be carried out at 730 mm. barometer reading, then according to (2):

$$\begin{aligned} 760 - 730.0 &= 30.0 \text{ mm.} \\ 30 \times 0.0453 &= 1.359^\circ \end{aligned}$$

In carrying out this distillation, therefore, in order to obtain the percentage distilled over, when the height of the barometer is 760 mm., the temperature of distillation must be taken at  $100 - 1.359 = 98.641^\circ$ , or approximately 98.6°, instead of 100°.

A. Spilker has shown, however, that the following artificially prepared mixtures all give the limits of boiling point required for a 90% benzol:

- (a) 82.0 % benzene + 18.0 % toluene.
- (b) 92.2 % benzene + 7.8 % xylene.
- (c) 90.0 % benzene + 5.0 % toluene + 5.0 % xylene.
- (d) 84.0 % benzene + 13.0 % toluene + 3.0 % xylene.

Of these mixtures only (d) corresponds in composition with an average commercial 90% benzol.

### Method of Testing Drip Oils<sup>1</sup>.

#### Apparatus:

The apparatus shall consist of the following standard parts:

##### I. Flask:

The distillation flask shall be a standard 100 c.c. Engler distilling bulb, having the following dimensions (see Stillman's Engineering Chemistry):

Angle of tubulure.....	75.0°
Diameter of bulb.....	6.5 cm.
Length of neck.....	15.0 cm.
Diameter of neck.....	1.6 cm.
Surface of oil to tubulure.....	9.0 cm.
Length of tubulure.....	10.0 cm.

A variation of four per cent. (4%) from the above measurements is allowable.

##### II. Thermometer:

Gas-filled centigrade thermometer constructed according to the following specifications:

<sup>1</sup>Owing to the high cost (at this time of writing) of benzol and toluol, the specifications for testing drip oils are very rigid. The method given is much used by the Reviser of this Section and was supplied him by C. C. Tutweiler.

1. To be made of Corning or Jena glass.
2. Diameter of stem not less than 6.5 mm. nor more than 8.5 mm.
3. Length of the thermometer not less than 335 mm. nor more than 400 mm.
4. Length of thermometer between 0° mark and 220° mark not less than 230 mm. nor more than 245 mm.
5. Length of bulb to capillary not less than 12 mm. nor more than 16 mm.
6. Diameter of bulb at centre of same not less than 5.25 mm. nor more than 6.25 mm.
7. Mercury column to rise from 10° to 95° in not more than 6 nor less than 4 seconds when plunged into boiling water.
8. To be correct within  $\frac{1}{10}^{\circ}$  at 100° and at 200° when tested against a similar thermometer certified by the Bureau of Standards.
9. Arranged for  $3\frac{1}{2}$  immersion with graduations starting above immersion line.

### III. Condenser:

Liebig glass condenser and tube as follows:

Length of body of jacket.....	300-400 mm.
Width of body of jacket.....	25-40 mm.
Length of inner tube.....	450-500 mm.
Width of inner tube, which is to be either straight or provided with an enlarged upper end, between 12 and 25 mm. at each end.	
Width of end of inner tube.....	12-35 mm.

### IV. Stands:

Two iron stands provided respectively with one universal clamp for holding the condenser, and one light grip arm with cork-lined clamp for holding the bulb.

### V. Burner:

A Bunsen burner shall be employed.

### VI. Cylinders:

Glass cylinders of 25 c.c. capacity graduated to  $\frac{1}{5}$  c.c. shall be used in collecting and measuring the fractions distilling up to 135°C.

## Setting Up Apparatus.

The apparatus is set up so that the top of the bulb of the thermometer is opposite the middle of the tubulure. All connections should be tight.

## Distillation Test.

One hundred cubic centimetres of the oil measured at 15.5°C. are placed in the bulb and, after adjusting the thermometer, condenser, etc., the distillation is commenced, the rate being so regulated that the stream flows at the maximum rate possible while producing distinct drops from the end

of the condenser tube. Cold water should be passed through the condenser during the distillation. The receiver is changed as the mercury column just passes the  $135^{\circ}\text{C}$ . fractionating point.

### Fractions.

The distillate shall be collected in two fractions. One fraction representing the amount distilling to  $135^{\circ}\text{C}$ .; the other representing the amount distilling above  $138^{\circ}\text{C}$ . The amounts coming over, up to the following points should be noted, reading to 0.1 c.c. at  $135^{\circ}\text{C}$ . and 1 c.c. at the other points.

$100^{\circ}\text{C}$ .	$150^{\circ}\text{C}$ .
$110^{\circ}\text{C}$ .	$160^{\circ}\text{C}$ .
$120^{\circ}\text{C}$ .	$170^{\circ}\text{C}$ .
$130^{\circ}\text{C}$ .	$180^{\circ}\text{C}$ .
$135^{\circ}\text{C}$ .	$190^{\circ}\text{C}$ .
$140^{\circ}\text{C}$ .	$200^{\circ}\text{C}$ .

All fractions, before being read, must be brought to  $15.5^{\circ}\text{C}$ .

### Water.

Should the distillate coming off to  $135^{\circ}\text{C}$ . contain water, the water and oil shall be allowed to separate by subsidence and the amount of water and oil shall be read separately to one-tenth cubic centimetre (0.1 c.c.). The observed amount of the oil fraction shall then be corrected by dividing the same by the figure obtained by deducting the per cent. of water as regards volume of the 100 c.c. sample from 100%. The result shall be taken as being the corrected amount of oil distilling to  $135^{\circ}\text{C}$ .

**Estimation of Aromatic Hydrocarbons in Admixture with Paraffins.**—According to Kraemer and Spilker,<sup>1</sup> this estimation is carried out as follows: 200 grm. of the sample are treated in a capacious separating funnel with 500 grm. of fuming sulphuric acid containing 20% of anhydride, and shaken for a quarter of an hour, avoiding undue heating; the whole is then allowed to stand for 2 hours. The layer of sulphuric acid is drawn off and the operation repeated twice with the same quantities of fuming acid. After treatment with 1,500 grm. of acid as above, everything except the paraffins, carbon bisulphide and naphthenes has usually dissolved. The oil remaining in the funnel is collected and the whole of the acid used is poured, with shaking, upon an equal weight of chopped ice contained in a 3-litre flask, taking care that the temperature does not rise above  $40^{\circ}$ . The solution is then boiled over a naked flame and the free hydrocarbons present are distilled off and collected in a 100 c.c. separating funnel, the distillation being continued until 50 c.c. of water have passed over after the oil. In this manner all the oil dissolved by the sulphonic acids or mechanically mixed with the liquid is recovered and, after the water has been drawn off, is added

<sup>1</sup>Muspratt, *Handbuch der technischen Chemie*, 4th ed., Vol. 8, p. 43.

to the main quantity. The whole of the oil is then again repeatedly shaken with 30 grm. of fuming sulphuric acid containing 20% of  $\text{SO}_3$ , until no further reduction in volume takes place, after which it is finally washed with a small quantity of water. The weight of oil obtained, divided by 2, gives the percentage of paraffins in the sample. This is scarcely more than 1% in the case of 90%, 50% and 0% benzols; toluol usually contains none; xylol, on the contrary, often contains up to 3% of paraffins.

**Estimation of Unsaturated Hydrocarbons in Aromatic Hydrocarbons.**—A measure of the quantity of unsaturated compounds (hydrocarbons of the ethylene and acetylene series, etc.), present in a crude benzol is afforded by titration with bromine. The bromine water formerly used for this purpose is best replaced by a solution of potassium bromide and bromate, which on addition of sulphuric acid, sets free 8.0 grm. of bromine per litre. The test is carried out by Frank in the following manner: 5 c.c. of the sample are added to 10 c.c. of dilute sulphuric acid (1:5), contained in a 50 c.c. vessel provided with a glass stopper, and  $N/10$  bromide-bromate solution, containing 9.9167 grm.  $\text{KBr} + 2.7833$  grm.  $\text{KBrO}_3$  per litre, is added from a burette until, after 5 minutes, shaking, bromine still remains. The titration is finished when the floating oil remains orange-red in colour after standing for 15 minutes and when 1 drop gives a dark blue colouration with freshly prepared potassium iodide-starch paper. The quantity of bromine used (1 c.c. = 0.008 grm. Br) should be given as such. To obtain accurate results, a preliminary estimation is first made, and then two exact estimations, the mean of which is taken. Pure benzene and pure toluene should show a marked bromine reaction after the addition of 0.1 c.c. of the bromine solution, whilst 90 and 50% benzols will decolourise, on an average, 0.6 c.c. of the reagent, but seldom more than 1 c.c. Commercial xylene absorbs 2% of bromine in a few minutes and considerably more on standing for some time.

#### ERRATA IN VOL. III.

Page 50, line 12, for "Leu" read "Leo." Line 22 for "in" read "of."

Page 54, line 10, for "Beaumé" read "Baumé."

Page 67, bottom line, for "Beaumé" read "Baumé."

Page 72, line 11, for "that of No. 2" read "that a No. 2."

Page 74, line 2, for "the Marcusson" read "Marcusson."

Page 76, line 4, for "with" read "of."

Page 78, line 11, for "ane" read "are."

Page 107, line 6, for "40" read "50."

Page 109, line 17, delete "to."

Page 114, line 9 from bottom, for "evapourating" read "evaporating."

Page 116, line 10 from bottom, for "evapouration" read "evaporation."

Page 122, instead of lines 17 to 20 inclusive read "The following abridged description of the apparatus devised by Sir Frederick Abel is taken from Schedule 1 of the Petroleum Act 1879. It sufficiently indicates the method of its use."

Page 139, line 2, for "Agnew" read "Angew."



Page 154, line 1, after "Viscosimeter" insert "(Fig. 7)."

Page 154, lines 23 to 25, delete "The cut was loaned by Bullock and Crenshaw of Philadelphia" and "shown in Fig. 6."

Page 174, line 6, for "or the radius" read " $r$ , the radius."

Page 176, line 15 from bottom, insert "is" after "crucible."

Page 178 line 20 for " $K_2PtCl_2$ " read " $K_2PtCl_6$ ."

Page 179, line 4 from bottom, for "generally" read "general."

Page 198, in table for "Naphthaline" read "Naphthalene," for "Renene" read "Retene."

Page 199, in table systematic name for cymene should be "methylisopropylbenzene" not "methylpropylbenzene."

Page 209, line 10, for "in" read "of."

Page 210, line 5 from bottom, for "tetra-*p*-quinonisol" read "*p*-methoxytetrahydroquinoline;" and in the same line for "be shaken into" read "and."

Page 224, line 8 from bottom, for "nitrofication" read "nitration."

Page 228, line 2, for "fullows" read "follows." Line 20 from bottom, for " $CS_2(C_6H_5NH.NH_2)_2$ " read " $CS_2(C_6H_5NH.NH_2)_2$ " and delete comma after phenylhydrazine.

# NAPHTHALENE AND ITS DERIVATIVES.

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By W. A. DAVIS.

**Naphthalene in Coal Gas.**—Several papers dealing with the estimation of naphthalene in coal gas have been published since the appearance of Vol. III. In all cases the methods proposed for the purpose differ only slightly from those described in this volume.

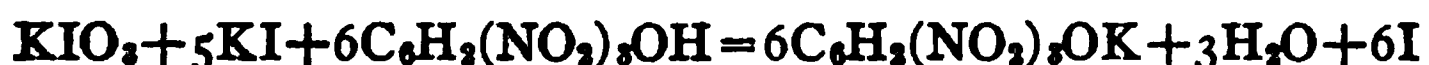
Albrecht and Müller<sup>1</sup> recommend a modification of Rutten's process<sup>2</sup> which is itself a modified form of Colman and Smith's method. 2.5 gm. of picric acid are placed in approximately equal parts in 2 wash bottles of 100 c.c. capacity, 25 c.c. of water are added to each bottle and the contents shaken until the water is saturated and the 2 wash bottles are connected with the glass tubes in contact so as to prevent the gas from acting on the rubber connection. The gas is passed through the solution at the rate of from 40 to 50 litres per hour until from 0.05 to 0.2 gm. of naphthalene has been apparently absorbed. The contents of the flasks are then washed into a 250 c.c. measuring flask and the free picric acid dissolved by adding water and gently warming. After cooling the solution is diluted to 250 c.c. and 200 c.c. are titrated with *N*/10 potassium hydroxide using lacmoid as indicator. At the same time a similar quantity of a solution containing 2.5 gm. of picric acid in 250 c.c. is titrated similarly; the difference in the number of c.c. of potassium hydroxide required multiplied by the factor  $\frac{5}{4} \times 0.0128$  gives the quantity of naphthalene present in grams. The accuracy of the method is shown by means of tests in which known weights of naphthalene were volatilised in dry nitrogen gas. In applying the method to coal gas, care must be taken to remove tar, cyanogen, hydrogen sulphide and ammonia. The use of scrubbing apparatus containing wood shavings, moist iron ore, etc., is shown to give quite unreliable results. Good results, however, are obtained by simply washing the gas in 2 wash bottles containing dilute sulphuric acid followed by two containing dilute potassium hydroxide.

From tests made by the authors cited, the higher percentage of naphthalene in crude gas from vertical retorts as compared with horizontal retorts (10.7 gm. per cubic inch, with a gas temperature of 71° compared with 8.6 gm. per cubic inch with a gas temperature of 54° for English coal and 8.6 gm. per cubic inch with a gas temperature of 60° for Upper Silesian coal) is due simply to the higher temperature and is not dependent on the class of coal employed.

<sup>1</sup> *J. Gasbeleucht.*, 1911, 54, 592.

<sup>2</sup> *J. Gasbeleucht.*, 1909, 52, 694.

A. Wein<sup>1</sup> has proposed the following method of working: about 40–50 litres of the gas are drawn by a filter pump through a solution of picric acid contained in a set of 3 washing flasks, which are kept well cooled during the absorption. The gas passes from the last flask through a cotton-wool filter, then through a flask containing concentrated sulphuric acid and thence to the meter and the filter pump. About 700 c.c. of picric acid solution containing 12 gramm. per litre are used. The connection between the first and second flask is provided with a by-pass so that after 20–25 litres have been passed the gas can be admitted directly to the second flask. When sufficient gas has been passed, air is sucked through so as to sweep out all naphthalene from the tubes, the flasks are then closed and heated for 30 minutes in a water-bath at 40°. After cooling, the whole of the precipitate consisting of naphthalene picrate contaminated with tar and ammonia is collected on a filter and placed together with the filter paper in an Erlenmeyer flask with 500 c.c. of water acidified with sulphuric acid so as to fix the ammonia. The whole is boiled gently so as to decompose the naphthalene picrate and the naphthalene is drawn with a current of air through flasks containing a picric acid solution of known strength. These flasks are then closed and heated at 40° and after cooling, the naphthalene picrate is filtered off and the picric acid in the filtrate estimated volumetrically. For this purpose, 50 c.c. of the solution are mixed with 10–12 c.c. of a solution containing 100 gramm. of potassium iodide and 30 gramm. of potassium iodate per litre and the iodine liberated according to the equation



is titrated with sodium thiosulphate. Wein's process seems to be more tedious and to present few, if any, advantages over the ordinary method of working.

Schlumberger<sup>2</sup> has also suggested a modification of Colman and Smith's method which he states is quite satisfactory. Exactly 2.7 gramm. of picric acid are placed in a 10-bulb absorption tube and made up with water to about 100 c.c. The gas is passed through saturated citric acid to free it from ammonia, then through the absorption tube and finally through the meter. 300–400 litres of gas should pass in 10–15 hours. The contents of the tube are washed into a 250 c.c. flask, diluted to the mark and, after stoppering, the flask is heated 30 minutes at 40° with frequent shaking and then cooled. The contents are filtered through asbestos and the picric acid in 100 c.c. of the filtrate determined by adding 25 c.c. of potassium iodide-iodate solution (150 gramm. iodide, 30 gramm. iodate, 400 c.c. of water) and estimating the liberated iodine with thiosulphate. 2.7 gramm. of the same picric acid have been previously dissolved in 250 c.c. of water and 100 c.c. titrated in the same way. The difference between the 2 titrations gives the picric acid combined

<sup>1</sup> *J. Gasbeleucht.*, 1911, 54, 891.

<sup>2</sup> *J. Gasbeleucht.*, 1912, 55, 1257.

with the naphthalene. The presence of benzene in the coal gas does not interfere with the estimation of naphthalene. Schlumberger gives data for the vapour pressure of naphthalene at different temperatures between 0° and 50° and the corresponding number of grams of naphthalene per 100 cubic metres.

Temperature	Vapour pressure in millimeters of mercury	Grams of naphthalene per 100 cubic metres
0	0.006	4.51
5	0.010	7.38
10	0.021	15.23
15	0.035	24.95
20	0.054	37.83
25	0.082	56.48
30	0.133	90.10
35	0.210	139.96
40	0.320	209.88
45	0.518	334.39
50	0.815	517.94

Laurain<sup>1</sup> describes two methods, in use at the Paris gas works, of estimating the amount of naphthalene in coal gas. Both depend upon direct cooling and condensation and are not chemical in their nature; being open to objection on different grounds they are not described here.

**Estimation of Naphthalene in Spent Oxide.**—According to W. C. Davis<sup>2</sup> the separation of naphthalene from spent oxide by the process proposed by White and Ball,<sup>3</sup> which consists in volatilising the naphthalene in a current of hot air, gives very low results, owing to the incomplete volatilisation of the hydrocarbon. It is better to separate the naphthalene by steam distillation and then to estimate it by the picrate process. The details are as follows: 10 grm. of the sample are weighed into a Wurtz flask and subjected to steam distillation, the steam being passed through a second Wurtz flask, heated to 100° and containing 50 c.c. of *N*-sulphuric or citric acid, then into a condenser and finally into a receiver consisting of a wide-mouthed bottle. The whole apparatus is sealed by placing at the exit a wash bottle containing 25 c.c. of a saturated picric acid solution. The distillation is complete in about 10 minutes. The naphthalene in the condenser is then melted out, the picric acid in the final washing flask is washed into the receiver and sufficient solid picric acid added to make the whole solution saturated; the receiver is closed with a rubber stopper and heated in the water-bath until a clear solution is obtained. The solution is cooled, with occasional shaking, and the excess of picric acid estimated by titrating with *N*/10 sodium hydroxide in the usual way.

It is necessary, as indicated in the details given above, to have the solution containing the naphthalene saturated with solid picric acid before heating to convert the naphthalene into picrate; unless this precaution is observed, slightly low results are obtained, owing to the solubility of naph-

<sup>1</sup> *J. Gas Lighting*, 1912, 118, 984.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1914, 33, 1120.

<sup>3</sup> *J. Gas Lighting*, 1904, 88, 262; Lunge's *Technical Methods of Chemical Analysis*, ii, 803.

thalene picrate in water. Experiments made with weighed quantities of pure naphthalene showed that the process described above is sufficiently reliable for all practical purposes.

**Estimation of  $\beta$ -Naphthol.**—J. M. Wilkie<sup>1</sup> has published a careful investigation of Messenger and Vortmann's iodometric method (Vol. III, p. 258) as applied to the estimation of phenols. In the case of  $\beta$ -naphthol, when its cold aqueous solution is treated with  $N/10$  iodine an almost quantitative yield of 1-iodo-2-hydroxynaphthalene is obtained; but in the presence of a slight excess of alkali hydroxide over that corresponding with the formation of  $C_{10}H_7ONa$ , a crystalline colourless product is no longer obtained but the green amorphous compound of Messenger and Vortmann. In carrying out the quantitative process, variable results are obtained with  $\beta$ -naphthol according to the excess of iodine used, a result which differs from that obtained with phenol and salicylic acid, in which cases the absorption of iodine is independent of the alkali and iodine, provided that the excess exceeds 60%. The quantitative process is, however, quite satisfactory when carried out in *practically neutral* solution as follows:

1.44 gm. of the naphthol is dissolved in 10 c.c. of  $N/1$  sodium hydroxide; if the solution is diluted to 200 c.c. it is  $N/10$  to iodine. 10 c.c. are then transferred to a Jena glass bottle, 150 c.c. of water added at the ordinary temperature and 4 c.c. of  $N/10$  sulphuric acid so as to leave a feebly alkaline solution. 20 c.c. of  $N/10$  iodine are added and after standing in a bath of water at  $55^\circ$  to  $65^\circ$ , some sulphuric acid is added and the residual iodine titrated with thiosulphate in the usual manner.

Under the conditions given the interaction takes place practically quantitatively according to the equation:



**Pharmacopœia Requirements.**—The British Pharmacopœia, 1914, gives the melting point of  $\beta$ -naphthol as  $122^\circ$ , and the following test for the absence of  $\alpha$ -naphthol; 0.1 gm. dissolved in 10 c.c. of boiling water yields with 10 drops of an aqueous solution (1 in 30) of ferric chloride a white precipitate which becomes brown but not violet. The pure naphthol should give no appreciable ash.

#### ERRATA IN VOL. III.

Page 250, line 21, "pages 274 and 275" should read "pages 245 and 276."

Page 258, line 19 "page 274" should read "pages 245 and 276."

Page 260, line 9 from bottom, for "Vol. 5" read "p. 559."

<sup>1</sup> *J. Soc. Chem. Ind.*, 1911, 30, 398.

# PHENOLS.

By S. S. SADTLER.

**Estimation of Phenol in Crude Carbolic Acid and Tar Oils.**—A method given by J. M. Weiss<sup>1</sup> depends upon the determination of the sp. gr. and solidifying point of a distillation fraction of the separated tar acids. These characters for pure phenol (synthesised from benzene), *o*-cresol (extracted from a mixture of cresols and purified by crystallisation and fractional distillation) and a mixture of *m*- and *p*-cresol (separated by fractionation from commercial mixture) are as follows:

	Phenol	<i>o</i> -Cresol	Mixture of <i>m</i> - and <i>p</i> -cresol
Solidif. pt., °C.....	40.5	27.75	below -10
Sp. gr. at 25°/25° C.....	1.0429	1.0313	1.0313
B. p. range, °C.....	First drop at 179 1% at 180 92% at 181 100% at 182	First drop at 189 19% at 190 93% at 191 100% at 192	First drop at 198 6% at 200 81% at 201 100% at 202

In carrying out an estimation, 300 c.c. of the tar acids separated in the usual manner are distilled in a flask fitted with a Hempel tube until the vapour temperature is 170°. Any phenol in the aqueous distillate is separated and returned to the distilling flask, and two further fractions are collected, viz., 170°–190° and 190°–202°. The last-named is redistilled and all coming over below 197° is added to the 170°–190° fraction, which now should contain all the phenol and no homologues higher than the cresols. The solidifying point and sp. gr. of this fraction are determined, whereupon the percentage of phenol may be estimated from the following data, showing the percentages of phenol corresponding with different sp. gr. for mixtures of different solidifying points.

Phenol content of mixture	Mixtures solidifying at				
	Below 0°	0°–5°	5°–10°	10°–15°	15°–23°
%	sp. gr. at 25°/25° C.	sp. gr. at 25°/25° C.	sp. gr. at 25°/25° C.	sp. gr. at 25°/25° C.	sp. gr. at 25°/25° C.
0	1.032	1.038	1.039	1.040	1.041
5	1.035	1.040	1.041	1.042	1.403
10	1.040	1.042	1.043	1.044	1.045
20	1.043	1.045	1.047	1.048	1.048
30	1.047	1.048	1.050	1.051	1.052
40	1.049	1.052	1.053	1.054	1.055
50	.....	.....	1.055	1.057	1.058
60	.....	.....	.....	.....	1.061

<sup>1</sup> *J. Gas Lighting*, 1913, 122, 820.

For mixtures solidifying above  $23^{\circ}$ , the phenol content may be estimated from the solidifying point alone, viz.,  $23.5^{\circ}$ , 70%;  $29.5^{\circ}$ , 80;  $32.75^{\circ}$ , 85;  $35.5^{\circ}$ , 90 and  $37.75^{\circ}$ , 95% of phenol. The figures given whilst not accurate for all possible mixtures of phenol and the cresols, cover satisfactorily all those likely to be obtained in practice and the results (referred to the original material) will be accurate to within 0.2–1.5 %, according to the proportion of tar acids present.

**Effect of Temperature, Acid Concentration and Time on the Bromination of Phenol in Quantitative Estimations.**—Rhodes and Redman<sup>1</sup> have shown that if the concentration of the phenol be about  $N/100$ , the reaction with bromine (hypobromite solution or a bromide-bromate mixture) is complete in about 1 minute when thoroughly shaken and only tri-bromophenol is formed as a white flocculent precipitate. Experiments by Redman, Weith and Brock,<sup>2</sup> on the effects of varying experimental conditions on the reaction have shown that for the complete bromination of phenol in 1 minute at  $22^{\circ}$  in a solution containing free acid in a concentration of  $0.8N$ , a 2% excess of free bromine is sufficient. It is stated that in this way phenol may be estimated to within 0.00005 gm.

The solutions used are  $N/10$  sodium thiosulphate and an  $N/10$  solution of either hypobromite or bromide-bromate, 20% KI and 1/2% starch solutions.

The procedure is as follows: Into a 500 c.c. bottle, fitted with a ground glass stopper, put 60 c.c. water, 5 c.c. hydrochloric acid (sp. gr. 1.2) and then add 15 c.c. of the unknown phenol solution which is to be determined and which has previously been diluted to about  $N/10$ . If the solution is weaker than  $N/10$  no previous dilution is required. Add quickly enough  $N/10$  hypobromite or bromide-bromate solution to make the solution yellow and then add in addition 10% of the amount already added. Place the stopper in the bottle and shake continuously for 1 minute. Add to the solution in the bottle 5 c.c. potassium iodide solution (10%) and again shake for 3 minutes. Wash down the stopper and sides of the bottle and titrate the solution with the  $N/10$  thiosulphate, using starch solution as an indicator. The starch must not be added until enough thiosulphate has been run in to make the solution almost colourless. The quantity of thiosulphate used represents the quantity of free iodine and therefore the quantity of excess bromine. The difference between this quantity and the known quantity of bromine added gives the amount of solution present. Each c.c. of  $N/10$  bromine used up is equivalent to 0.00156 gm. of phenol.

**The Value of the Higher Phenols in Wood-preserving Oils**—2 gm. each of heavy creosote oil and of phenols extracted from the same were exposed by Cabot<sup>3</sup> on a watch glass at a temperature of from  $50^{\circ}$ – $55^{\circ}$  for 200 hours and the loss of weight noted at stated intervals. The residue

<sup>1</sup> *J. Ind. Chem.*, 1912, 4, 655.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1913, 5, 389–393.

<sup>3</sup> *J. Ind. Eng. Chem.*, 4, 206, 1912.



fully followed 1.74 gm. of trinitro-*m*-cresol are obtained for each 1.0 gm. of *m*-cresol present in the mixture, whatever the composition of the latter. The presence of even 10% of phenol does not diminish the accuracy, as the picric acid which is formed remains in solution; but the method must not be applied to mixtures containing very large amounts of phenol, which, however, do not often occur in practice. In such samples the presence of phenol is detected by the boiling point, and also by the fact that the nitro-compound does not remain solid in the steam-oven at 95° to 100°, but melts, or at any rate, forms a soft paste. Xylenols, which sometimes occur in commercial cresols, behave in a similar manner; the nitro-compound either liquefies when warm or refuses to set in the cold. But a cresol which distils for the most part between 190° and 200°, and, therefore, contains scarcely any phenol or xyleneol always yields a pale yellow crystalline mass, the weight of which when divided by 1.74 gives the weight of *m*-cresol in the mixture, the error being within 1%. The amount of nitric acid used is considerably more than is needed for the nitration and oxidation and good results can be obtained with average cresols containing 35 to 60% of *m*-cresol, when only 70 c.c. of nitric acid are used; but if this is done the action often occurs so suddenly that there is scarcely time to mix the sulphonic acid with the nitric acid and place the flask on one side; explosions have even been known to occur under these conditions. The recognised quantity of 90 c.c. of acid is, therefore, adhered to, and is poured, all at once, into the flask as quickly as possible, a flask having a very wide neck being used.

F. Russig and G. Fortmann<sup>1</sup> have described a method which is used in France. This is not so simple or rapid as Raschig's method, but gives rather higher results, probably because the nitration is more complete; it is also inapplicable to mixtures containing more than 10% of phenol or xylenols. 50 gm. of the cresol are weighed into a small conical flask and mixed with 125 gm. of sulphuric acid of sp. gr. 1.84. The temperature of the mixture rises spontaneously to between 60° and 70°, and further warming is unnecessary. After standing for 1-2 hours, the sulphonic acid is nitrated in a tubulated retort of 1 litre capacity, placed on a sand-bath; the neck of the retort is connected to a wash bottle and this, in turn, to a good draught. 400 c.c. of nitric acid of sp. gr. 1.38 are placed in the retort, heated to 60°, and the flame then removed. A cylindrical dropping-funnel without a neck is fixed in the tubulure of the retort by a rubber stopper and the small conical flask in which the sulphonation was effected is placed upside-down over the funnel in such a way that the contents are only delivered slowly and are similarly emptied from below. The sulphonic acid is allowed to gradually drop into the hot nitric acid during a period of 1½-2 hours; it is thus completely nitrated and oxidised; the oxidation is accompanied by a violent development of heat and evolution of nitrous fumes. About

<sup>1</sup> *Z. anorg. Chem.*, 1901, 14, 157.

20 minutes after the conclusion of the action, the contents of the retort are poured into a dish containing 200 c.c. of water and the retort is rinsed out with a further 200 c.c. After standing over night, the crystalline mass is crushed in the dish, filtered on a hardened filter on the pump, washed with a further 200 c.c. of water, and weighed. When treated in this manner 50 gm. of pure *m*-cresol yield 87.8 gm. of trinitro-*m*-cresol, being 175.6 %, whereas by Raschig's method only 174.0% is obtained on the weight of the original cresol.

### Creosote.

The following methods of the New York Testing Laboratory are recommended by the writer for creosote oils.

**Sp. Gr.**—By pyknometer at 38° compared with water at the same temperature.

**Sulphonation.**—10 c.c. of the total distillate up to 315° are placed in a flask and warmed with four to five volumes of concentrated sulphuric acid to 60° and the whole transferred to a graduated separating funnel. The flask is rinsed three times with small quantities of concentrated sulphuric acid and the rinsings added to the contents of the funnel, which is then stoppered and shaken, cautiously at first, afterwards vigorously, for at least 15 minutes and allowed to stand over night. The acid is then carefully drawn down into the graduated portion of the funnel to within 2 c.c. of where the unsulphonated residue shows. If no unsulphonated residue shows, the acid should be drawn down to 2 c.c. In either case the test should be carried further as follows: Add about 20 c.c. of water and allow to stand  $\frac{1}{2}$  hour. Then draw off the water as close as possible without drawing off any supernatant oil or emulsion; add 10 c.c. of concentrated sulphuric acid and allow to stand for 15–20 minutes. Any unsulphonated residue will now separate out clear and give a distinct reading. If under  $\frac{2}{10}$  of a c.c. it should be drawn down into the narrow part of the funnel to just above the stopcock where it can be estimated to  $\frac{1}{100}$  of a c.c. (0.01 c.c.). The volume of residue thus obtained is calculated on the original oil.

**Tar Acids.**—50 c.c. of the distillate to 315° to which 40 c.c. of a solution of sodium hydroxide (19%) having a sp. gr. of 1.15, is added, is warmed slightly and placed in a separating funnel. The mixture is vigorously shaken, allowed to stand until the oil and soda solutions separate and the soda solution containing most of the tar acids drawn off. A second and third extraction is then made in the same manner, using 30 and 20 c.c. of the sodium hydroxide solution respectively. The three extracts are united in a 200 c.c. graduated cylinder and acidified with dilute sulphuric acid. The mixture is then allowed to cool and the volume of the tar acids noted. The results shown should be calculated on the original oil.

**Distillation.**—100 gm. of the oil are distilled in an 8-ounce glass retort. The lower end of the bulb of the thermometer is placed  $\frac{1}{2}$  in. above the

surface of the oil and the distillation conducted at the rate of 1 to 2 drops per second.

**Coke Test.**—In making the coke determination hard glass bulbs are to be used.

Warm the bulb slightly to drive off all moisture, cool in a desiccator and weigh. Again heat the bulb by placing it momentarily in an open Bunsen flame, place the tubulure underneath the surface of the oil to be tested and allow the bulb to cool until sufficient oil is sucked in to fill the bulb about two-thirds full. Any globules of oil sticking to the inside of the tubulure should be drawn into the bulb by shaking or expelled by slightly heating it and the outer surface should be carefully wiped off and the bulb reweighed. This procedure will give about 1 grm. of oil. Cut a strip of thin asbestos paper about 1 in.  $\times$   $\frac{1}{4}$  in., place it around the neck of the bulb and catch the two free ends close up to the neck with a pair of crucible tongs. The oil should then be distilled off, as in making an ordinary oil distillation, starting with a very low flame and conducting the distillation as fast as can be maintained without spurting. When the oil ceases to come off, the heat should be increased until the highest temperature of the Bunsen flame is reached, the whole bulb being heated red hot until evolution of gas ceases and any carbon adhering to the outside of the tubulure is completely burned off. The bulb should then be cooled in a desiccator and weighed and the percentage of coke residue calculated to water free oil.

Coal-tar creosote oils have no greater coke than 3 %.  
Water-gas creosote oils have more coke than 3 %.

**Antiseptic Properties of Creosote** (K. V. Kharichkov<sup>1</sup>).—After removing the phenols, bases and unsaturated hydrocarbons from creosote by the usual methods, its antiseptic properties were tested on cultures of *Merulius lacrimans*, *Penicillium glaucum* and a parasitic fungus from decaying strawberries. The results show that the removal of the above constituents hardly influences the antiseptic properties of creosote.

**Antiseptic Tests of Wood-preserving Oils.**—A. L. Dean and C. R. Downs<sup>2</sup> have made experiments with *Polystictus versicolour*, which was obtained in pure culture from decaying wood. This is the fungus that destroys 75% of the broadleaf timber used for ties. The culture medium was prepared by adding 0.5% cane sugar and 0.5% asparagine to germinated bean extract and then stiffened by adding 1.5% agar-agar. The creosote oils were emulsified by grinding with an equal weight of gum arabic, adding water from time to time. A small piece of the medium to be inoculated was cut out and laid to one side, the transferred mycelium and agar from the stock culture placed in the cavity and the piece of creosoted medium replaced on top. In this way the mycelium was buried and if it grew up through and vegetated on the surface, there could be no question that the antiseptic was

<sup>1</sup> J. Russ. Phys. Chem. Soc., 44, 345-348.

<sup>2</sup> Orig. Com., 8th Intern. Congr. Appl. Chem., 13, 103-210.

insufficient. The results showed that coal-tar creosote is a stronger antiseptic than water-gas tar creosote, and that the latter is more effective than the liquid oils of the anthracene fraction of coal tar. The greater value of the coal-tar creosote appears to depend upon the presence of the tar acids and especially upon the tar bases. The water-gas tar creosote was almost identical in antiseptic power with the coal-tar oil which had had its acids removed. Allman's work indicated that the oils remaining in wood treated with coal-tar creosote were almost free from tar acids after a few years and that the lighter hydrocarbons may all disappear. Loss of antiseptic power from disappearance of tar acids cannot take place with water-gas tar oils, since they are free from phenols from the beginning. Since the amount commonly injected into wood is 10 pounds or more per cubic foot, the difference in antiseptic power between coal-tar oils and water-gas tar oils is not of great significance.

**Note on the Rideal-Walker Phenol Control.**—A new method is presented by Walker and Weiss,<sup>1</sup> of insuring the purity of phenol used in determining the bactericidal efficiency of disinfectants and to show that the presence of cresols probably accounts for the varying results obtained. Different mixtures of cresol in 0–30% strength with synthetic phenol were made and the lowering of the melting point was found to be constant, for any particular degree of this impurity, regardless of the varying proportions of the three isomeric cresols. A curve plotted showed the solidifying point to be a linear function of the per cent. of phenol up to at least 30% cresol. From this if the solidifying point is known, the degree of cresol contamination can be determined. The bactericidal efficiency of cresol is three times that of phenol. The various estimations made with synthetic phenol agree closely with the calculated theoretical figures. It is well known that phenol crystals are usually contaminated by cresols to such an extent as to make them unreliable for purposes of bactericidal control. This impurity depresses the coefficient of the disinfectant. The bromine titration is insufficient to insure the purity of the phenol. The solidifying point is the best test. No phenol showing a solidifying point of less than 40° should be used for purposes of bactericidal control.

**Detection of Natural Asphaltum and Petroleum Pitch in Residues from the Distillation of Coal Tar.**<sup>1</sup>—A method of detecting natural asphaltum or petroleum pitch in the residues from the distillation of coal tar is based upon the fact that distillates of the latter (consisting in the main of aromatic hydrocarbons) are converted by sulphuric acid almost quantitatively into sulphonic acids which are soluble in water, whereas the distillates from natural asphaltum or petroleum pitch are only affected to a limited extent by this treatment. If, however, large quantities (*e.g.*, up to 20%) of these bituminous products are present in coal-tar pitch, the distillation causes decomposition, with the formation of unsaturated hydrocarbons capable of being attacked by sulphuric acid. The following method of separating the compounds

<sup>1</sup> *J. Frank. Inst.*, 174, 101–12.

<sup>2</sup> F. Schwarz, *Chem. Rev. Fell. Ind.*, 1913, 20, 28–30.

which combine with sulphuric acid obviates the necessity of distillation: 10 grm. of the pitch are heated to  $160^{\circ}$ – $180^{\circ}$  in an oil bath, then stirred for 5 minutes with 4 c.c. of concentrated sulphuric acid and the temperature kept at  $180^{\circ}$  until all sulphurous acid and excess of sulphuric acid have been expelled. The mass is then thoroughly ground up with 40 grm. of bone charcoal, and extracted in a Soxhlet apparatus with petroleum spirit of low boiling point, the extract evaporated, the residue taken up with more petroleum spirit, the solution filtered and evaporated and the residue weighed. Any sulphur present is removed by treating the residue (without stirring) with acetone, filtering the solution, evaporating the filtrate and again weighing the residue. The amounts of constituents not attacked by sulphuric acid varied as follows in the case of the samples examined: coal-tar pitches, 0.10–0.20; natural asphaltums, 1–16 (usually 3–8); and petroleum pitches, 6–36% (usually 15–30%). If the result obtained as above greatly exceeds 0.2%, the presence of natural asphaltum or petroleum pitch is indicated.

**Application of the Dimethyl Sulphate Test for Detecting Small Amounts of Petroleum or Asphalt Products in Tars.**<sup>1</sup>—The material is not distilled to coke and a test made on the total distillate, as in the Sommer method, but into three fractions:  $270$ – $315^{\circ}$ ,  $315$ – $350^{\circ}$ , and  $350$ – $375^{\circ}$ . The asphalt distillate concentrates in these fractions, especially the last, and can easily be detected by taking 4 c.c. of the fraction, mixing with 6 c.c. dimethyl sulphate in a 10 c.c. cylinder graduated to 0.2 c.c. and shaking. After standing, the layer of insoluble petroleum can be read. The method does not give quantitative results, but when the grades of asphalt and tar oil in a mixture are known, tests on like laboratory mixtures enables one to determine within narrow limits the per cent. of each constituent in the material under investigation.

#### ERRATA IN VOL. III.

Page 263, line 11, for "dihydroxyanthraquinone" read "dihydroxyanthraquinone."

Page 273, line 14 from bottom, for Vol. 5 read Vol. 6.

Page 278, line 15, for "naphthalquinone" read "naphthaquinone." Line 18, insert brackets round "diphenylene ketone."

Page 293, line 17 from bottom, for "absorption" read "absorption."

Page 301, line 16 from bottom, for "Nortmann" read "Vortmann."

Page 308, line 5, insert comma after "sample." Line 7 from bottom, for "theire" read "their."

Page 314, line 9 from bottom, for "0.7379" read "0.7397." Line 4 from bottom for "with" read "within."

Pages 319 and 320, in several places, for "pyridin" read "pyridine."

Page 321, line 3 from bottom, for "chlorid" read "chloride."

Page 324, line 15, for "page 160" read "page 25."

Page 345, line 20, for "Gassetta" read "Gazzetta."

Page 348, line 5 from bottom, for " $20^{\circ}$ " read " $-20^{\circ}$ ."

Page 364, line 4, in table, for "105" read "195."

Page 383, line 21 from bottom, for "dimethynaphthalenes" read "dimethylnaphthalenes."

Page 390, heading of Table, for "Beaumé" read "Baumé."

<sup>1</sup> Charles S. Reeve and Richard H. Lewis, *J. Ind. Eng. Chem.*, 5, 293–295.

# AROMATIC ACIDS.

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By EDWARD HORTON.

## Phenol-*p*-sulphonic Acid.

**Estimation.**—The following volumetric method is described by Smith and Frey.<sup>1</sup> A quantity of the sample corresponding with 0.18–0.20 grm. of phenol-*p*-sulphonic acid is dissolved in 50 c.c. of water in a stoppered long-necked 250 c.c. flask. To this are added 50 c.c. of an aqueous solution containing 2.7833 grm. of potassium bromate and about 40 grm. of potassium bromide per litre. 5 c.c. of hydrochloric acid (D 1.18) are then added, the flask stoppered to prevent loss of bromine and the mixture kept at 20°–25° for not less than 10 and not more than 15 minutes, during which time no turbidity should be produced. Dibromophenolsulphonic acid is formed by the action of the free bromine, the excess of which is determined by titration with standard thiosulphate solution after the addition of potassium iodide. The method is accurate to  $\pm 0.5\%$ .

## Benzoic Acid and Its Derivatives.

**Commercial Benzoic Acid.**—For the detection of halogens in the benzoic acid of commerce, Wende<sup>2</sup> gives the following test: A mixture of 0.1 grm. of the sample with 0.5 grm. of yellow mercuric oxide is heated in a dry test-tube, the latter being constantly turned over a flame about 1 cm. high. When the action is over, about 10 c.c. of dilute nitric acid are added, the whole heated nearly to boiling and filtered. The filtrate should not give more than a slight opalescence with silver nitrate solution.

The British Pharmacopœia 1914 requires benzoic acid to conform to the following standard:

“When 0.5 grm. is heated in a closed crucible with twice its weight of calcium carbonate, the mass dissolved in diluted nitric acid, and solution of silver nitrate added, not more than the slightest cloudiness results (absence of chlorobenzoic acid). Yields no characteristic reactions for oxalates. Does not develop the odour of benzaldehyde when warmed with its own weight of potassium permanganate and 10 times its weight of dilute sulphuric acid (absence of cinnamic acid). Arsenic limit 2 parts per million.”

**Reactions and Detection.**—Since the publication of Vol. III several authors have published new methods for the detection of benzoic acid, or

<sup>1</sup> *J. Amer. Chem. Soc.*, 1912, 34, 1040.

<sup>2</sup> *Apoth. Zeit.*, 1914, 29, 157.



modifications of old ones. The test devised by Mlle. Anna Jonescu seems to meet with considerable commendation, being applied or recommended by Halphen, Marchadier, Thomann, Denigès, Biernath, Philippe and Fleury. On the other hand, Fischer and Gruenert state that it is far inferior to the modified Mohler method.

Fleury<sup>1</sup> points out that the Jonescu reaction takes place very slowly in cold solutions, whilst heat is liable to carry it too far and so to cause failure. He hastens the action by the addition of a trace of ferrous sulphate to act as catalyst. 10 c.c. of the solution to be tested (containing 1–5 mg. of benzoic acid) are treated with 3 drops of a solution of ferric chloride (sp. gr. 1.260, containing about 26% of the anhydrous salt) diluted 1 to 10, then with 3 drops of a solution of hydrogen peroxide (12 vol.) also diluted 1 to 10, and finally with 3 drops of 3% solution of ferrous sulphate. The reagents should be added in the order named, shaking after each addition. In about 30 seconds action commences, and the violet colouration attains its maximum in 5–10 minutes. The test is sensitive to 0.0002 gram. of benzoic acid.

Denigès<sup>2</sup> publishes the following modification of Jonescu's method. To 4 c.c. of an aqueous solution supposed to contain benzoic acid, 0.2 c.c. of 20% (by volume) acetic acid, 0.2 c.c. of ferric chloride solution (dilute) and 0.2 c.c. of hydrogen peroxide solution (one volume) are added and the mixture is boiled for 10–15 seconds. A violet colouration is obtained even when the solution contains not more than 0.0005 gram. of benzoic acid per 1 c.c. In cases where smaller quantities are to be detected a blank experiment should be made simultaneously, both test-tubes being heated in boiling water for the same length of time.

Halphen<sup>3</sup> points out that if in preparing the solution for the Jonescu test ammonia is used to neutralise the acid before evaporating to dryness, 0.001 gram. of benzoic acid will fail to give the test, whilst by using sodium hydroxide a sharp indication is obtained.

von der Heide and Jakob<sup>4</sup> have described the following method to detect benzoic acid in wine. A sample of the wine is made alkaline and evaporated until all the alcohol has been driven off. The residual solution is acidified, submitted to steam distillation, and the distillate extracted with ether. The ethereal solution is evaporated and the residue tested by Robin's modification of Mohler's method (Vol. III, p. 410). The method is stated by Polenske<sup>5</sup> to be trustworthy.

For the detection of benzoic acid in milk Revis<sup>6</sup> has devised the following process. At least 100 c.c. of the milk are diluted with an equal volume of water, 5 c.c. of a 10% solution of sodium carbonate are added, and the mix-

<sup>1</sup> *J. Pharm. Chim.*, 1913 [vii], 8, 460.

<sup>2</sup> *Bull. Soc. Pharm. de Bord.*, 1911, 249; *Pharm. J.*, 1911, 87, 201.

<sup>3</sup> *Matières grasses.*, 1910, 3, 1761.

<sup>4</sup> *Zeitsch. Unter. Nahr. Genussm.*, 1910, 19, 137.

<sup>5</sup> *Arbeit. Kaiserl. Gesundheitsamte*, 1911, 38, 149.

<sup>6</sup> *Analyst*, 1912, 37, 346.



ture is heated in boiling water for 2-3 minutes. 10 c.c. of a 20% solution of calcium chloride are added, the heating is continued until the casein is completely coagulated, the liquid cooled and filtered, and the filtrate made neutral to litmus paper with hydrochloric acid. To the neutral filtrate 10 c.c. of copper sulphate solution (as made for Fehling's solution) and 10 c.c. of potassium hydroxide solution (containing 31.18 grm. per litre) are successively added and the liquid again filtered. The filtrate is transferred to a separating funnel, acidified with hydrochloric acid and shaken with 50 c.c. of ether. The aqueous solution is run off, the ether washed three times with a little water, 10 c.c. of water and a drop of phenolphthalein solution are added, and a saturated solution of barium hydroxide is run in gradually, with shaking, until a permanent pink colour is produced. The aqueous layer is now filtered into a porcelain basin, evaporated to about 5 c.c., filtered into a test-tube and 1% acetic acid added until the liquid is decolourised. Two more drops of the acetic acid are then added, and 1 drop of a freshly prepared neutral solution of ferric chloride (10%). With as little as 0.02% of benzoic acid the characteristic precipitate of ferric benzoate is obtained. In examining cream 50 c.c. are diluted with water to 200 c.c. and then treated as above.

Philippe<sup>1</sup> extracts the benzoic acid from the milk by a similar method and identifies it by Robin's or Jonescu's test.

According to Hinks<sup>2</sup> 0.01% or more benzoic acid in milk or cream can be detected as follows: 25 c.c. of the milk or from 10 to 20 grm. of the cream are heated with an equal volume of concentrated hydrochloric acid until the curd has completely dissolved. The liquid is cooled, shaken with 25 c.c. of a mixture of light petroleum (2 vols.) and ether (1 vol.), the ethereal solution separated and shaken with 1 drop of ammonia and 5 c.c. of water. The aqueous layer is now separated, heated on a water-bath for a few minutes to expel the excess of ammonia and then tested with ferric chloride solution. On adding the ammonia, ammonium benzoate is precipitated and this test although less characteristic is more sensitive than the ferric chloride test.

Fischer and Gruenert<sup>3</sup> have continued their work on the detection of benzoic acid in meat and fats. They find that the methods of Halphen and Robin which are applicable to butter are entirely inapplicable to meats and other fats. On the other hand, von der Heide and Jakob's modification of Mohler's method gave a sharp indication with as little as 0.01% of benzoic acid in 50 grm. of substance. The authors prefer to extract the preservative from meats by the method previously described (Vol. III, p. 411), but for butter and margarine they recommend the following process: 50 grm. of butter are introduced into a 300 c.c. Erlenmeyer flask, treated with 150 c.c. of 1% sodium hydrogen carbonate solution and boiled for 5 minutes with

<sup>1</sup> *Mitt. Lebensmittel-unters. Hyg.*, 1911, 2, 377.

<sup>2</sup> *Analyst*, 1913, 38, 555.

*Zeitsch. Nahr. Genussm.*, 1912, 20, 580.

frequent shaking. If necessary a blast of air is used from time to time to prevent frothing. The hot liquid is transferred to a separating funnel and the aqueous layer drawn off, neutralised with  $N/2$  sulphuric acid solution, using methyl-orange as indicator, and clarified by adding 10 c.c. of Fehling's copper sulphate solution and 10 c.c. of potassium hydroxide solution (containing 31.15 gm. per litre). The liquid, which should be neutral or faintly acid, is filtered, the filtrate acidified with dilute sulphuric acid and extracted with ether. The ethereal extract is washed, evaporated and the residue tested by von der Heide and Jakob's method.

Robin states<sup>1</sup> in reference to his modification of Mohler's method that since salicylic acid and other phenolic derivatives respond to the test, these must be removed by dissolving the benzoic acid extract in dilute sulphuric acid, adding 10% potassium permanganate solution until the red colouration becomes permanent after heating at  $80^{\circ}$ , and then extracting with ether and proceeding with the test (Vol. III, p. 410).

For the detection of benzoic acid in butter, methods are described by Marchadier<sup>2</sup> and Biernath<sup>3</sup> in which the sample is distilled with water, a little sulphuric acid and a small quantity of pumice-stone and the distillate tested by Jonescu's method. Biernath states that the reaction is retarded by mineral acids, volatile organic acids and alcohol.

Friese<sup>4</sup> and Volhase<sup>5</sup> have described other methods of detecting benzoic acid in fats, but these are similar to that of Fischer and Gruenert.

Lythgoe and Marsh<sup>6</sup> have observed that when the ethereal extract of coffee or pure coffee extract is treated with ferric chloride solution in the usual manner for the detection of benzoic acid, a precipitate is obtained which differs from ferric benzoate in colour, and yields crystals different from those of benzoic acid on sublimation. The ammonium salt of the substance which produces this precipitate is distinguished from ammonium benzoate in that it gives precipitates with manganese, nickel, magnesium, calcium, barium and strontium. Accordingly when looking for benzoic acid in coffee extract these authors recommend that the acid solution should be extracted several times with ether, the ether extract washed with water and extracted with ammonia. The ammoniacal solution is evaporated to a small volume, adding ammonia to prevent development of acidity, and treated with a solution of manganese sulphate. It is then filtered and the filtrate tested for benzoic acid with ferric chloride solution.

A new test for benzoic acid has been discovered by Schmatolla.<sup>7</sup> If 20 c.c. of a solution containing benzoic acid are treated with 5 c.c. of hydrogen peroxide solution, and then with freshly prepared solution of 5 gm. of ferrous

<sup>1</sup> *Ann. Falsif.*, 1913, 6, 277.

<sup>2</sup> *Ann. Falsif.*, 1911, 4, 28.

<sup>3</sup> *Apoth. Zeit.*, 1912, 27, 192.

<sup>4</sup> *Pharm. Zentr.*, 1911, 52, 1201.

<sup>5</sup> *Chem. Zeit.*, 1913, 37, 312.

<sup>6</sup> *J. Ind. Eng. Chem.*, 1911, 3, 842.

<sup>7</sup> *Pharm. Zeit.*, 1913, 57, 947.

**sulphate** and 5 grm. of boric acid in 100 c.c. of water, a blue or greenish-blue colour appears in a few seconds.

### Estimation.

**Volumetric Methods.**—An iodometric method of estimating benzoic acid has been described by Remy.<sup>1</sup> The acid (0.05–0.5 grm.) is dissolved in 30 c.c. of 50% alcohol. 5–10 c.c. of 5% potassium iodide solution and an equal volume of 5% potassium iodate solution are added and the liberated iodine titrated with thiosulphate solution. The benzoic acid is converted into mono-iodobenzoic acid, and one molecule of benzoic acid is equivalent to one atom of iodine.

For the estimation of benzoic acid in benzoates Lyons<sup>2</sup> dissolves 0.25 grm. of the salt in 10 c.c. of water in a separating funnel, acidifies with 25 c.c. of *N*/10 sulphuric acid solution and extracts four times with chloroform (which must be neutral). The chloroform is run into a second separating funnel, washed with 20 c.c. of water, transferred to a flask and titrated with *N*/25 alkali solution using methyl-red as indicator. The end point of the titration is indicated by the appearance of a yellow colour in the aqueous layer after shaking with the chloroform.

Whilst extraction with chloroform can be applied to the estimation of benzoic acid in cranberries, Folin and Flanders<sup>3</sup> found that certain precautions have to be taken in the case of ketchups, from which chloroform extracts other acids also. 25 grm. of the ketchup are placed in a 50 c.c. beaker, treated with 2 c.c. of concentrated nitric acid and about 0.2–0.3 grm. of sodium nitrite added in small portions, the mixture being well stirred after each addition. The liquid is rinsed into a 500 c.c. separating funnel with the help of 200 c.c. of saturated ammonium sulphate solution, and is then extracted five times with chloroform (50 c.c., 35 c.c., 25 c.c., 25 c.c., 25 c.c.). The chloroform is run into another separating funnel and shaken with 200 c.c. of a saturated solution of sodium chloride made faintly acid with hydrochloric acid. It is then transferred to a third separating funnel, again shaken with 200 c.c. of the acidified salt solution, and finally run into a 500 c.c. Erlenmeyer flask and titrated with standard alcoholic sodium ethoxide solution in the presence of phenolphthaleïn.

Cinnamic acid is not removed by the washing with salt solution, hence any present will be estimated with the benzoic acid. The sodium ethoxide solution is prepared by dissolving 2–3 grm. of sodium in a litre of absolute alcohol; it is standardised against benzoic acid in chloroform solution.

Raiziss and Dubin<sup>4</sup> sought for a solvent which would not form emulsions with urine. They found that toluene is preferable to the chloroform recom-

<sup>1</sup> *Apoth. Zeit.*, 1911, 26, 835.

<sup>2</sup> *J. Amer. Pharm. Assoc.*, 1912, 1, 526.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1911, 33, 1622.

<sup>4</sup> *J. Biol. Chem.*, 1915, 20, 125.

mended by Folin and Flanders. 100 c.c. of fresh urine are acidified with 1 c.c. of concentrated nitric acid, then saturated with ammonium sulphate (50–60 grm. being required) and extracted four times with toluene (50 c.c., 40 c.c., 30 c.c., and 30 c.c.). The toluene extracts are mixed and washed with 100 c.c. of saturated salt solution containing 0.05% of concentrated hydrochloric acid. The washing is repeated and then the benzoic acid in the toluene solution is titrated with  $N/20$  sodium ethoxide solution using phenolphthaleïn as indicator. The ethoxide solution is prepared by dissolving 2.3 grm. of sodium in alcohol and diluting the solution to 2000 c.c. Hippuric acid is not extracted by toluene under the above conditions.

McAbee<sup>1</sup> has applied the provisional A. O. A. C. method of estimating sodium benzoate to ketchups containing added known weights of the salt and has shown that the method is reliable.

To estimate salicylic and benzoic acids and saccharin in fruit juices, jams, and lemonades, van Raalte recommends<sup>2</sup> boiling these substances for 5 hours with dichloroethylene followed by titration with  $N/10$  alkali solution and phenolphthaleïn. Then the neutral aqueous liquid, after separation from the dichloroethylene, is examined for the two acids and saccharin. The latter can be extracted with ether after addition of phosphoric acid.

In a report<sup>3</sup> on cooperative work on the determination of sodium benzoate in jams, jellies, and salt codfish, Dunbar advocates making the former two substances alkaline with milk of lime instead of sodium hydroxide, the latter being used with codfish. The sodium benzoate is then extracted with a definite volume of water, of which an aliquot part is saturated with sodium chloride, filtered, acidified and extracted with chloroform, the chloroform solution being evaporated and the residue titrated.

Van der Laan and Tijdens<sup>4</sup> recommend extracting benzoic acid from foods by means of benzene for quantitative estimation.

Polenske<sup>5</sup> has described a method of estimating benzoic acid in cranberries.

**Gravimetric Methods.**—Hinks<sup>6</sup> states that the benzoic acid present in milk may be estimated by heating 25 c.c. with hydrochloric acid in a reflux apparatus, extracting the cooled solution three times with 20 c.c. of a mixture of ether (1 vol.) and light petroleum (2 vols.) and shaking the separated ethereal solutions with 10 c.c. of water and 1 drop of ammonia; this extraction is twice repeated. The mixed aqueous portions are then acidified with hydrochloric acid, extracted three times with the ethereal solvent, the extracts evaporated at ordinary temperature and the residue dried in a desiccator to constant weight. The benzoic acid is then volatilised at  $100^{\circ}$  and its amount determined by the loss in weight.

<sup>1</sup> *J. Ind. Eng. Chem.*, 1910, 2, 544.

<sup>2</sup> *Chem. Weekblad.*, 1912, 9, 1004.

<sup>3</sup> *U. S. Dept. Agr. Bur. Chem., Bull.* 137, 108.

<sup>4</sup> *Chem. Weekblad.*, 1910, 7, 603.

<sup>5</sup> *Arbeit. Kaiserl. Gesundheitsamte*, 1911, 38, 149.

<sup>6</sup> *Analyst*, 1913, 38, 555.

Liverseege and Evers<sup>1</sup> have described an empirical method of estimating benzoic acid in milk, by which, however, only about 45% of the acid is obtained.

Hillyer<sup>2</sup> has devised a method of estimating benzoic acid in ketchups depending on the precipitation of the acid from alcoholic solution as silver benzoate and weighing as such. To estimate benzoic acid in chopped meat Krüger<sup>3</sup> recommends the following out of several modifications of the distillation method. 50 grm. of the chopped meat are mixed with enough sulphuric acid, making allowance for the moisture content of the sample, to have present 45 c.c. of 70% sulphuric acid. The mixture is heated until clear and then steam distilled (keeping the volume constant) until 500 c.c. of distillate have been collected. The cold distillate is filtered and the filter washed, the filtrate made faintly alkaline with sodium hydroxide solution and evaporated to small bulk on a water-bath. To remove impurities, a cold saturated solution of potassium permanganate is added until the red colour produced persists for 5 minutes. The excess of permanganate is destroyed with sodium sulphite solution and the liquid evaporated to 10 c.c. After cooling it is transferred to a separating funnel and acidified with dilute sulphuric acid (1:3). The manganese precipitate, remaining in the basin is dissolved in cold saturated sodium sulphite solution and sulphuric acid and transferred to the funnel. The liquid is extracted three times with an equal volume of a mixture of ether and light petroleum, the ethereal solution washed three times with 3 c.c. of water and dried with a small amount of powdered gum tragacanth. It is then allowed to evaporate spontaneously in a tared basin, dried and weighed. The results can be checked by subliming the product and reweighing or by titration. From 97 to 120% of the benzoic acid present is recovered by this method.

### Metallic Benzoates.

The British Pharmacopœia 1914 fixes the following standard of purity for the sodium and ammonium salts:

**Sodium Benzoate.**—"Loses not more than 4% of its weight when dried at 112°. 1 grm. of this dried salt heated to redness until gases cease to be evolved leaves an alkaline residue which treated with water, filtered and well washed, yields a clear solution requiring for neutralisation not less than 13.7 c.c. nor more than 13.9 c.c. of *N*/2 solution of sulphuric acid. Yields no characteristic reactions for copper, iron, potassium or carbonates, and not more than the slightest reactions for chlorides or sulphates. Lead limit 10 parts per million. Arsenic limit 2 parts per million."

**Ammonium Benzoate.**—"If 1 grm. is dissolved in 20 c.c. of water and excess of nitric acid added a crystalline precipitate of benzoic acid separates, the filtrate from which remains clear on the addition of solution of barium chloride, and does not become more than slightly opalescent on the addition of solution of silver nitrate. Lead limit 10 parts per million. Arsenic limit 2 parts per million."

<sup>1</sup> *J. Soc. Chem. Ind.*, 1913, 32, 319.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1909, 1, 538.

<sup>3</sup> *Zeitsch. Nahr. Genussm.*, 1913, 26, 12.

**Benzoic Aldehyde. Benzaldehyde.**

**Estimation. Volumetric Method.**—Dodge states<sup>1</sup> that benzaldehyde can be estimated by the following modification of Ripper's method. 0.15 gm. of the aldehyde is mixed in a flask with 25 c.c. of *N*/5 sodium hydrogen sulphite solution and dissolved by gentle shaking. The flask is corked and kept in ice-water for 1.5 to 2 hours. The solution is then titrated cold with *N*/10 iodine solution using starch as an indicator. The aldehyde can also be estimated by allowing about 1 gm. to stand at room temperature with 10 c.c. of 2.5 *N*-alcoholic potassium hydroxide solution for 24 hours and then titrating the free alkali. But oil of bitter almonds cannot be assayed by this method.

**Gravimetric Methods.**—The method described by Denis and Dunbar<sup>2</sup> has been studied both by Smith and by Woodman and Davis. Smith dealt with the application of the method to maraschino products. He found<sup>3</sup> that distillation in an atmosphere of carbon dioxide gave somewhat better results than in air, whilst distillation from strong sodium chloride solution gave results which were too high. Also that it is best to keep the volume of the solution during precipitation as small as possible, that the results were not affected by the presence of 20% of alcohol (by volume) and that larger amounts may be removed by distillation without affecting the estimation. The precipitate was filtered on two superimposed filter papers, one of which had been counterbalanced against the other, and was again used as a counterpoise after drying. The mean amount of benzaldehyde recovered was 88%.

Woodman and Davis<sup>4</sup> state that to obtain accurate results by the Denis and Dunbar method with small quantities the volume of the solution should not exceed 110 c.c. and the alcohol content should be between 8 and 12% by volume. According to these authors the method is not suitable for such small quantities of benzaldehyde as are present in maraschino cherries, for which they recommend a modified method. 100 c.c. of the liquor from maraschino cherries or 50 c.c. of maraschino liqueur, are diluted to 140 c.c. and 110 c.c. distilled off. After approximately determining the alcohol content in a small portion of the distillate 100 c.c. are mixed with alcohol or water sufficient to bring the alcohol content to about 10% by volume. The solution is then shaken vigorously for 10 minutes in a rubber-stoppered flask with 100 c.c. of the freshly prepared phenylhydrazine reagent (3 c.c. of glacial acetic acid mixed well with 40 c.c. of water and 2 c.c. of phenylhydrazine and filtered through several thicknesses of filter paper). The precipitate is collected in a tared Gooch crucible, washed first with cold water and then with 10 c.c. of 10% alcohol and dried either in a vacuum desiccator at 20 cm. pressure for 20–24 hours or in a vacuum oven at 70°–80°.

<sup>1</sup> Eighth Inter. Cong. App. Chem., Sect. VIII b. Orig. Comm. 17, 15.

<sup>2</sup> Vol. III, p. 419.

<sup>3</sup> U. S. Dept. Agr., Bur. Chem., Bull. 152, 192.

<sup>4</sup> J. Ind. Eng. Chem., 1912, 4, 588.



for 3 hours. The weight of precipitate obtained in a blank determination is deducted and the corrected weight multiplied by 0.5411 to obtain the weight of benzaldehyde. The method can be applied to almond extracts by using 10 c.c. of the extract diluted to 100 c.c., and 15 c.c. of the reagent. In maraschino cherries the benzaldehyde expressed in mg. per 100 c.c. of the liquor should not be more than two or three times the alcohol content expressed in percentage by volume.

According to Golse<sup>1</sup> the French official method of estimating hydrocyanic acid and benzaldehyde in liqueurs is untrustworthy, the chief objections being the use of insufficient alkali to fix the hydrocyanic acid and faulty conditions of precipitation of the aldehyde phenylhydrazone. The author recommends the following procedure: 200 c.c. of the liqueur are treated with 1 c.c. of sodium hydroxide solution (sp. gr. 1.32–1.36) in a 600 c.c. flask and distilled until 175 c.c. of distillate have been collected (*A*). The residual liquid in the flask is then cooled, 50 c.c. of 10% sulphuric acid solution are added slowly from a tap-funnel and the mixture again distilled 50 c.c. of distillate being collected in a receiver containing 5 c.c. of ammonia (*B*). The distillate (*A*) is now transferred to a distillation flask, 5 c.c. of the phenylhydrazine reagent added, the mixture diluted to 200 c.c., and 75 c.c. distilled over; this distillate contains traces of hydrocyanic acid and is added to the distillate (*B*). The lower end of the condenser is then closed and the flask heated on a water-bath until the hydrazone has been precipitated, 2 hours heating being usually sufficient. The precipitate is collected on a filter paper, washed with water and dissolved by treatment with 10 c.c. of alcohol followed by 20 c.c. of ether. The alcohol-ether solution is evaporated, the residue dried in *vacuo* and weighed. The weight  $\times 2.7$  gives the weight of benzaldehyde in a litre of the liqueur. The phenylhydrazine reagent is prepared by dissolving 1 gm. of phenylhydrazine in a mixture of 4 c.c. of glacial acetic acid, 2 gm. of sodium acetate and 20 c.c. of water, heating and shaking vigorously, adding 1 c.c. of sodium hydrogen sulphite solution and filtering. The presence of the sodium hydrogen sulphite prevents the oxidation of the phenylhydrazone during precipitation.

The distillate (*B*) is used for the estimation of the hydrocyanic acid.

Feinberg<sup>2</sup> has made an investigation of the methods of estimating typical aldehydes, and publishes results which show that for benzaldehyde the neutral sulphite method is better than that with bisulphite, and that precipitation with *p*-nitrophenylhydrazine gives better results than using *p*-bromophenylhydrazine, the neutral sulphite method being perhaps slightly less accurate than precipitation with *p*-nitrophenylhydrazine. The best results are stated to be obtained as follows: 25 c.c. of a 1% solution of the aldehyde in 12% acetic acid are diluted with 50 c.c. of water, and a solution

<sup>1</sup> *J. Pharm. Chim.*, 1915, 12, 44.

<sup>2</sup> *Eighth Int. Cong. Appl. Chem.*, 1912, Sect. 1, Orig. Comm. 1, 187.



of twice the theoretical quantity of *p*-nitrophenylhydrazine in 30 c.c. of 30% acetic acid is added. After standing for 5 hours the precipitate is collected on a tared, Gooch crucible, washed with 10% acetic acid until the washings no longer give a strong colour with dilute alkali, dried at 105°–110° and weighed. When the benzoic acid present is separately determined by titration with standard alkali solution and deducted from the weight of aldehyde (calculated from that of the hydrazone by multiplying by 0.4400) results showing an accuracy of 99% are obtained.

Hoffmeister has described<sup>1</sup> methods of estimating benzaldehyde in essential oils which depend on the removal of the aldehyde with sodium bisulphite, decomposition of the bisulphite compound with sodium hydroxide solution and subsequent precipitation of the aldehyde with phenylhydrazine.

**Assay of Benzaldehyde.**—Both Herzog<sup>2</sup> and Heyl<sup>3</sup> adversely criticise the method of the German Pharmacopœia, 5th Edition, for the detection of chlorine compounds in benzaldehyde. Heyl recommends instead that 10–15 drops should be mixed with 1–2 gm. of pure slaked lime, the mixture covered with a thin layer of lime and the whole ignited to redness. The residue is taken up with 5–6 c.c. of water, dissolved in nitric acid and tested with silver nitrate solution. 1 drop of monochlorobenzene, it is stated, can be detected in 50 gm. of benzaldehyde in this way.

### Saccharin.

**Commercial Saccharin.**—The British Pharmacopœia 1914 sets the following standard of purity for saccharin.

“1 gm. heated for 4 hours on a water-bath with 10 c.c. of a mixture of 4 volumes of sulphuric acid and 3 volumes of water completely dissolves, and when the solution is diluted with an equal volume of water and allowed to stand for 24 hours, no crystals separate. Gently warmed for a short time with sulphuric acid no blackening occurs. Ash not more than 0.5%.

**Detection of Saccharin in Foods and Beverages.**—The methods of detecting saccharin described since the publication of Vol. III, differ chiefly, as did those contained therein, in the process of isolation, the identification still being dependent on its conversion into salicylic acid.

Camilla and Pertusi<sup>4</sup> isolate saccharin from solid foods by digesting on a water-bath with 2% baryta solution and extracting the filtrate, after acidification with sulphuric or phosphoric acid, with a mixture of ether and benzene. A liquid is concentrated on a water-bath, treated with baryta-water, filtered, and the filtrate after acidifying extracted with the ether-benzene mixture.

<sup>1</sup> *Arch. Pharm. Inst. Univ. Berlin*, 1913, 10, 147.

<sup>2</sup> *Ber. Pharm. Ges.*, 1911, 21, 536.

<sup>3</sup> *Apoth. Zeit.*, 1912, 27, 49.

<sup>4</sup> *Giorn. Farm. Chim.*, 1911, 60, 385.

Durand<sup>1</sup> recommends the removal of salicylic acid, if present, by means of bromine. An aqueous extract of the sample to be tested is acidified with phosphoric acid and extracted with ether. The ethereal solution is filtered, evaporated to dryness in a nickel basin and a portion of the residue tested for salicylic acid. If the latter is present, the remainder of the residue is dissolved in hydrochloric acid, an excess of bromine added and the mixture filtered; the salicylic acid is thus completely removed as a bromine derivative. The filtrate is then rendered strongly alkaline with sodium hydroxide, evaporated to dryness, and the residue (or the residue from the ethereal solution if salicylic acid is not present) is fused with soda in the ordinary way for conversion into salicylic acid.

Genth, Jr.<sup>2</sup> extracts saccharin from carbonated beverages with ether, and previous to the extraction of the solution of the alkaline fusion with ether, he exactly neutralises it in the presence of ferric alum solution. The appearance of a violet colour at this stage, renders subsequent operations unnecessary.

Flamand states<sup>3</sup> that the method of extracting saccharin from beer by means of ether or light petroleum, does not give good results when a considerable amount of hops has been used, because the bitter resins extracted simultaneously mask the taste of the saccharin. This difficulty can be met by a preliminary extraction of the beer with benzene, which dissolves the resins, but very little saccharin.

Volhase states<sup>4</sup> that the salicylic acid method is preferable to the recognition of saccharin by conversion of its sulphur into sulphuric acid. Herzfeld and Reischauer,<sup>5</sup> however, use a modification of the latter test to detect saccharin in wine and beer. The residue from the ethereal extract is mixed with magnesium powder and heated cautiously to ignition, the product is dissolved in cold water, filtered, and the filtrate tested with sodium nitroprusside solution, a strong violet colour indicating saccharin.

A new test for saccharin has been described by Wauters<sup>6</sup> and used for the detection of this substance in beer. When saccharin is heated with sulphuric acid and diresorcinol, it yields a product which after treatment with water and filtration gives an intensely violet liquid.

An extraction apparatus for the detection of saccharin in beer has been described by Ledent.<sup>7</sup> It consists of a glass tube 90 cm. long and 1.5 cm. internal diameter fixed vertically and fitted by means of corks, at the top with a stoppered dropping funnel, and at the bottom with a narrow glass tube which is bent round so as to pass up parallel to the wide tube to a height of 35-40 cm. at which point it is bent round and cut off in such a way that the

<sup>1</sup> *J. Ind. Eng. Chem.*, 1913, 5, 987

<sup>2</sup> *Amer. J. Pharm.*, 81, 536.

<sup>3</sup> *Bull. Soc. chim. belg.*, 1913, 26, 477.

<sup>4</sup> *Chem. Zeit.*, 1913, 37, 426.

<sup>5</sup> *Naturwiss. Wochschr.*, 1913, 165.

<sup>6</sup> 7th Inter. Congr. Appl. Chem., London, 1910.

<sup>7</sup> *Analyst*, 1913, 18, 314.

liquid flowing from it can fall into a flask placed below. 50 c.c. of the beer are run into the wide tube and then so much ether that the beer begins to drop from the side tube. The rest of the beer is then run into the wide tube drop by drop. As the drops fall into the ether they are broken up and the saccharin is extracted, but there is no formation of emulsion, and no preliminary treatment of the beer such as defecation is necessary. If necessary the beer can be passed through the apparatus several times.

Commanducci publishes<sup>1</sup> a warning relative to the testing of sweetened foods and beverages for saccharin. He states that when solutions of dextrose and cane-sugar were extracted with a mixture of equal volumes of ether and light petroleum the residue obtained by evaporation of the ethereal extract when heated with sulphuric acid and resorcinol and subsequently treated with alkali and water gave a fluorescent solution the production of which has always been regarded as characteristic of saccharin. If, however, the ethereal extract is washed three or four times with water (which does not remove saccharin) the residue no longer shows this behaviour.

Camilla and Pertusi<sup>2</sup> have described a method of detecting dulcin, salicylic acid and saccharin in the presence of one another.

**Estimation.**—To estimate saccharin in foods rich in fat, starch and proteins, Tortelli and Piazza<sup>3</sup> recommend the following process. A weighed quantity of the sample is mixed with about 18 gm. of fine sand and 10 gm. of slaked lime (liquids are evaporated to the consistence of a paste after the addition of the sand and lime) and the mixture is extracted four times with quantities of 50 c.c. of boiling 95% alcohol, 10 c.c. of a saturated solution of sodium chloride being added each time. The alcoholic solution is filtered, the filter washed with a mixture of alcohol and sodium chloride solution, and the filtrate evaporated to about 80 c.c. When cold the residual liquid is mixed with 10 c.c. of saturated sodium chloride solution, and extracted several times with light petroleum. After the fatty substances have been thus removed, the liquid is heated on a water-bath until all traces of alcohol have been expelled; it is then cooled, acidified with sulphuric acid, and extracted several times with a mixture of equal volumes of ether and light petroleum. The ethereal extracts are washed once with water, filtered and evaporated and the residue weighed. If the substance known as "dulcin" or "sucrol" (*p*-phenetolecarbamide) is present it may be separated by extracting with ether before acidification. Dulcin melts at 173°, saccharin at 223°. When a trace of the former substance is suspended in water and heated with mercuric nitrate solution (free from nitric acid) a violet colouration develops within 15 minutes, and may be made more intense by addition of a small quantity of lead peroxide.

Possetto and Issoglio<sup>4</sup> separate the saccharin by dialysis. In the case of

<sup>1</sup> *Boll. chim. farm.*, 1910, 49, 791.

<sup>2</sup> *Giorn. Farm. Chim.*, 1911, 60, 385.

<sup>3</sup> *Zeitsch. Nahr. Genussm.*, 1910, 20, 489.

<sup>4</sup> *Giorn. Farm. Chim.*, 1912, 61, 5.

milk and milk preparations 50 c.c., of jams and fruit jellies 50 grm., and of candied fruits, sweets, or cocoa 30 grm., are made alkaline with sodium carbonate solution and dialysed for 12–24 hours. The yellow solution produced is acidified with phosphoric acid and extracted twice with ether. The ethereal solution is washed, filtered, evaporated and the residue tested for salicylic acid. If this be present it may be separated either by treating the original solution after dialysis with bromine water and filtering, or with permanganate and sulphuric acid and filtering after 12 hours standing, the saccharin being afterwards extracted with ether (after acidifying with phosphoric acid if bromine be employed).

Other methods are described by Condelli<sup>1</sup> and Karas.<sup>2</sup> A method of estimating saccharin and saponin in oil emulsions is published<sup>3</sup> by Carlinfanti and Marzocchi, and a colourimetric method of estimating saccharin in urine has been described by Bloor.<sup>4</sup>

Ceccherelli states<sup>5</sup> that in estimating saccharin treatment of the ether extract with potassium permanganate is not to be recommended, although it is useful in making qualitative tests. Gum tragacanth, extract of gentian and certain other substances after fusion with sodium hydroxide produce colourations with ferric chloride and may therefore interfere with this method of testing for saccharin. Tarugi and Lenci<sup>6</sup> have described the following test, based on the liberation of the amino-group. A minute quantity of saccharin, heated with a few drops of sulphuric acid until white fumes appear, then cooled, diluted with water, neutralised with soda and added to a solution of a crystal of phenol in sodium hydroxide solution, gives a blue colour on addition, drop by drop, of a fresh solution of sodium hypochlorite.

The author concludes that there is at present no satisfactory means of estimating saccharin, applicable to all cases, but the presence of this substance may be regarded as certain if the ether extract, after treatment with permanganate, yields a residue which glistens slightly, contains sulphur, yields an insoluble silver salt containing 37% of silver gives the reactions of salicylic acid after fusion with soda but not before, and also responds to the above test after hydrolysis.

## CINNAMIC ACID AND ITS DERIVATIVES.

### Cinnamic Acid. $\beta$ -Phenyl-acrylic Acid.

**Detection.**—For the detection of cinnamic acid in urine von der Heide and Jakob<sup>7</sup> proceed as follows. A portion of the urine is rendered alkaline, evaporated to a small volume, acidified and extracted with ether. The ethereal solution is shaken with dilute alkali solution. The aqueous alkaline

<sup>1</sup> *Staz. sperim. agrar. ital.*, 1914, 47, 308.

<sup>2</sup> *Zeitsch. Nahr. Genussm.*, 1913, 25, 559.

<sup>3</sup> *Boll. chim. farm.*, 1911, 50, 609.

<sup>4</sup> *J. Biol. Chem.*, 1910, 8, 227.

<sup>5</sup> *Ann. Falsif.*, 1915, 8, 109.

<sup>6</sup> *Rend. Soc. Chim. Ital.*, 1911, 7, 320.

<sup>7</sup> *Zeitsch. Unter. Nahr. Genussm.*, 1910, 19, 137.

solution is heated on a water-bath until all the dissolved ether has been expelled, cooled and treated with 1% potassium permanganate solution; the first few drops of the latter convert any cinnamic acid present into benzaldehyde which may be recognised by its odour. As little as 0.00001 grm. of the acid gives a distinct smell of benzaldehyde.

A similar method is recommended by Schenk and Burmeister.<sup>1</sup> The substance in which cinnamic acid is to be detected is acidified with phosphoric acid and extracted with ether; the ethereal solution is then shaken with sodium carbonate solution, the aqueous layer separated, extracted twice with ether (this is essential, particularly in the case of fruit juices, in order to remove small quantities of furfuraldehyde compounds), and very dilute potassium permanganate solution is added, drop by drop, until the pink colour is only just discharged. The solution is now extracted with ether, the ethereal solution treated with 10 drops of a 5% ethereal solution of phenol and allowed to evaporate at the ordinary temperature. On adding a few drops of concentrated sulphuric acid to the residue a yellow colouration is obtained, even when the quantity of benzaldehyde formed from the cinnamic acid is too small to be identified by its odour. The furfuraldehyde compounds which may be present give, if not removed completely, a faint orange colouration which cannot be mistaken for that yielded by benzaldehyde.

Tunmann has devised<sup>2</sup> a micro-sublimation method of detecting cinnamic acid, especially in resins.

**Estimation.**—The method previously described by De Jong (Vol. III, p. 438) has been modified by him<sup>3</sup> in order to facilitate the combination of cinnamic acid with bromine. The acid is dissolved in sodium hydroxide solution and reprecipitated with hydrochloric acid. The resulting magma is treated with *N*/50 aqueous solution of bromine until the yellow colouration produced persists for 5 minutes. Then excess of potassium iodide solution is added and the free iodine titrated.

Bongault and Mouchel-la-Fosse<sup>4</sup> for the estimation of cinnamic in the presence of benzoic acid make use of the action between the former acid and sodium hydrogen sulphite. The acid is allowed to combine with a known volume of a standardised solution of the sulphite, the excess of which is then titrated with standard iodine solution.

### Cinnamic Aldehyde.

**Oil of Cinnamon. Oil of Cassia.**—The standard of purity required for cinnamon oil has been considerably modified by the latest edition of the British Pharmacopœia (1914). The latter states that oil of cinnamon is

“Yellow when freshly distilled, gradually becoming reddish. Sp. gr. 1.000 to 1.030; optical rotation  $-0.5$  to  $-1^{\circ}$ ; ref. index at  $25^{\circ}$  1.565 to 1.580. Soluble in 3 to 4 parts of

<sup>1</sup> *Pharm. Zeit.*, 1915, 60, 213.

<sup>2</sup> *Pharm. Zentr. h.*, 1913, 54, 133.

<sup>3</sup> *Rec. trav. chem.*, 1911, 30, 223.

<sup>4</sup> *Compt. rend.*, 1913, 156, 396.

alcohol (70%). 1 drop dissolved in 5 c.c. of alcohol (90%) assumes a pale green, but not a blue or brown colouration, on the addition of 1 drop of T. Sol. of ferric chloride [5%] (absence of cinnamon leaf oil and cassia oil). Contains from 55% to 65% of cinnamic aldehyde as determined by the following test:

To 10 c.c. of the oil add 70 c.c. of an aqueous solution (1 in 5) of sodium sulphite and sufficient solution of phenolphthalein to give a well-marked pink colouration. Heat the mixture on a water-bath, shake well and neutralise with acetic acid diluted with twice its volume of water; repeat the heating and neutralisation until no further pink colouration is developed, the time occupied being from 30 to 45 minutes. The oily layer which separates on standing, cooled to 15°.5, measures not more than 4.5 or less than 3.5 c.c. (presence of 55% to 65% of cinnamic aldehyde.)"

Cripps and Brown<sup>1</sup> estimate the essential oils in spices (particularly carraway and cinnamon) by heating the latter at 150°–160° (in the case of cinnamon) in a current of air which is afterwards passed through a heated combustion tube, the carbon dioxide formed being absorbed and weighed in the usual way. The weight of carbon found multiplied by 100/80 gives the weight of cinnamon oil.

**Adulterations of Oil of Cinnamon.**—Hill has pointed out<sup>2</sup> the value of a determination of the refractive index in detecting adulteration of cinnamon-bark oil. Of six samples of the genuine Ceylon oil of the finest quality, the ref. index at 25° varied only between 1.5727 and 1.5767 except for one sample which was more than 9 years old and was very resinous; this gave 1.5797. Two samples of cinnamon-bark oil distilled in England gave the values 1.5614 and 1.5752 respectively. The author gives values for other specimens and for cinnamon-leaf and cassia oils, cinnamic aldehyde, eugenol, pinene and phellandrene, which show that the genuine cinnamon-bark oil is distinguished from cassia oil and cinnamic aldehyde by a low sp. gr. (below 1.04 at 15°), a low ref. index (below 1.58 at 25°), a low aldehyde content (below 65%) and by affording a green colour with ferric chloride solution (cassia oil gives a chocolate brown colour). Adulteration with cinnamon-leaf oil can be recognised by an unduly high proportion of eugenol.

**Adulterations of Oil of Cassia.**—In the technical valuation of cassia oil, the cinnamic aldehyde is absorbed and the volume of the residue measured. Parry states<sup>3</sup> that most of the cassia oil arriving in London at the present time (1912) is adulterated with resin. Consequently the unabsorbed portion of the oil obtained in the assay has a much higher sp. gr. than cinnamic aldehyde so that an apparent content of 80% (by volume) of cinnamic aldehyde represents a considerably lower actual percentage by weight.

### Coumarin.

A method of detecting coumarin in vanilla extracts is described under "Vanillin."

<sup>1</sup> *Analyst*, 1909, 34, 519; 1910, 35, 392.

<sup>2</sup> *Chem. and Drug.*, 1910, 76, 59.

<sup>3</sup> *Perfum. and Essent. Oil Rec.*, 1912, 3, 46.



**Estimation.**—Obermayer<sup>1</sup> gives the following method of estimating coumarin in *Melilotus vulgaris* and *officinalis*. 10 gm. of the ground air-dried sample are extracted with ether in an extraction apparatus, and the ether is then evaporated in a 500 c.c. flask. The residue is treated with 300 c.c. of calcium chloride solution (1000 gm. in 3 litres) and distilled until the mass shows signs of solidifying. The heat should be regulated so that the operation lasts fully an hour. The distillate is diluted to a definite volume and then filtered. An aliquot portion of the filtrate is mixed with zinc sulphate solution, and then with excess of standard potassium permanganate solution and boiled on an asbestos plate for 10 minutes. After cooling, the liquid is filtered through an asbestos filter and the precipitate washed with water. The excess of permanganate in the filtrate and washings is determined in the usual manner by titrating with oxalic acid. The titre of the permanganate solution is best verified by a check experiment with pure coumarin.

### Aromatic Balsams.

**Gum Benzoin.**—Reinitzer states<sup>2</sup> that in addition to the benzoates of benzoiresinol and siaresinotannol Siam benzoin contains the benzoate of a previously unknown resin-alcohol, *lubanol*. The British Pharmacopœia (1914) gives the following test for Sumatra Benzoin:

“When 0.5 gm. is slowly heated to about 40° with 10 c.c. of solution of potassium permanganate an odour of benzaldehyde is evolved (distinction from Siam benzoin). Not more than 15% insoluble in alcohol (90%). Ash not more than 5%.”

**Assay.**—Cocking and Kettle<sup>3</sup> give the following method to estimate balsamic acids. 5 gm. are extracted with alcohol in a Soxhlet apparatus and the extract hydrolysed with alcoholic potassium hydroxide. The alcohol is evaporated, the residue dissolved in 100 c.c. of water and treated with a slight excess of hydrochloric acid, 5 gm. of light magnesium oxide and 20 c.c. of xylene. The whole is boiled under a reflux condenser for an hour, cooled, the aqueous portion filtered off and the insoluble matter boiled twice with 100 c.c. of water which is allowed to cool before filtering. The combined aqueous extracts are shaken out once with ether, then the balsamic acids are liberated by the addition of hydrochloric acid and removed by ether. The latter is distilled off, the residue dried in a vacuum over sulphuric acid and weighed. To estimate the cinnamic acid, the ethereal residue is left over night in contact with excess of a 5% solution of bromine in carbon tetrachloride and the excess is driven off by evaporation on a water-bath. The residue is evaporated several times with ether dried as before and

<sup>1</sup> *Zeitsch. anal. Chem.*, 1913, 172.

<sup>2</sup> *Arch. Pharm.* 1914, 252, 341.

<sup>3</sup> *Proc. Brit. Pharm. Conf.*, 1914, 13.



weighed. The amount of cinnamic acid is calculated from the increase of weight, one mol. of the acid absorbing two atoms of bromine.

The "free" balsamic acids are estimated by boiling the powdered drug with water, magnesium oxide and xylene and proceeding as above. The acid and ester values are determined on the alcoholic extract of a separate portion of the drug.

## CINNAMIC BALSAMS.

### Peruvian Balsam.

**Analysis.**—The British Pharmacopœia 1914 gives the following description and method of assaying Peruvian balsam:

"Insoluble in water; soluble in chloroform. 1 volume is soluble in 1 volume of alcohol (90%), but on the further addition of 2 or more volumes of alcohol, the whole becomes turbid. Sp. gr. between 1.140 and 1.158. Does not diminish in volume when shaken with an equal bulk of water (absence of ethylic alcohol). When tested by the following method it yields not less than 57% of cinnamein, the saponification value of which is not less than 235.

"Dissolve 1 gram. of the balsam in 30 c.c. of ether and shake in a separating funnel with two successive quantities of 20 c.c. and 10 c.c. of  $N/2$  solution of sodium hydroxide. Separate the alkaline solutions, mix and shake with 10 c.c. of ether. Add the second ethereal solution to that previously obtained. Wash the mixed ethereal solutions with two successive quantities of 5 c.c. of water. Transfer the ethereal solution thus washed to a tared wide-mouthed flask, evaporate at a gentle heat until the odour of ether has disappeared, add 1 c.c. of absolute alcohol, dry at  $100^{\circ}$  for half an hour and weigh. The weight of the cinnamein thus obtained is not less than 0.57 gram. To this residue add 20 c.c. of  $N/2$  alcoholic solution of potassium hydroxide, and 20 c.c. of alcohol (90%). Attach a reflux condenser, boil for half an hour, and titrate back with  $N/2$  solution of sulphuric acid, solution of phenolphthalein being used as indicator. Each gram of the residue thus treated requires not less than 8.4 c.c. of the alkaline solution for complete saponification (corresponding to a saponification value of not less than 235)."

To estimate cinnamein Lehmann and Müller recommend<sup>1</sup> the following method. 5 gram. of water are mixed with 2.5 gram. of the balsam in a 75 c.c. bottle, 30 c.c. of ether are added and the mixture shaken for 1 minute. 5 gram. of sodium hydroxide solution are then added and the mixture again shaken for 1 minute. The bottle is securely corked and set aside bottom upwards for 10 minutes. The cork is then carefully loosened and the aqueous portion allowed to run away till only 3 c.c. are left. 0.5 gram. of gum tragacanth is then added to the contents of the bottle and the whole shaken. After 5 minutes the clear ethereal solution is run into a tared wide-mouthed flask and its weight ( $w$ ) noted. The solvent is then distilled off, the residue dried at  $100^{\circ}$  for 30–45 minutes and its weight ( $w'$ ) determined. The percentage of cinnamein ( $x$ ) in the balsam is given by the following equation:  $x = (30w'/w - w')40$ . In this method the device of running most of the

<sup>1</sup> Arch. Pharm., 1912, 250, 1.

alkaline solution out of the inverted bottle is criticised as impractical by Frommé<sup>1</sup> who recommends fixing all the solution with gum tragacanth.

For the iodine number of the cinnamein from reliable Peru balsam Jensen found<sup>2</sup> the values 23.8 and 25.5 as against 1.5 for the synthetic ester. Upon fractional distillation of the cinnamein, the first 30% is optically active when derived from the true balsam, but inactive when obtained from the synthetic ester. This author states that benzyl benzoate has sp. gr. 1.121, saponification number 264.1, whilst for benzyl cinnamate the values are 1.098 and 235.3, respectively.

According to Stocker<sup>3</sup> there are undoubtedly pure and genuine balsams on the market which will not dissolve (1 grm.) to a clear solution in a solution of 3.0 grm. of chloral hydrate in 2 grm. of water. He suggests that the test should be modified by using 3.5 grm. of chloral hydrate.

**Adulterations of Peruvian Balsam.**—K. Dieterich<sup>4</sup> has examined samples of genuine Peru balsam which gave the following values: sp. gr. at 15°, 1.160; acid value 74.02–76.92; saponification value 214.34–243.07; iodine value 22.07 to 25.87; cinnamein 56.56–77.56%; saponification value of the cinnamein 253.61; iodine value of the cinnamein 7.48–7.91; resin esters 24.95%; and insoluble in ether 2.45–4.38%. The results obtained from artificial and “synthetic” balsams, as a whole, differed considerably from these limits, although individual values were frequently normal. The author finds that only the following identification tests are distinctive: Hager’s petroleum spirit test; determination of the solubility in alcohol, chloroform, chloral hydrate and carbon bisulphide; the nitric acid test; the zone reactions (Vol. III, p. 458) and the qualitative tests of the Swiss Pharmacopœia. He gives the following new colour test. 1 drop of the sample is shaken with 5 c.c. of light petroleum, and about half the liquid poured off. The remainder is mixed with 5 c.c. of ether and shaken with a few drops (10 to 15) of sulphuric acid, added drop by drop, when genuine Peru balsam gives a violet to blue colouration, whilst artificial products give quite different colours. This reaction is due to the cinnamein of the balsam.

When distilled in a current of steam, Peru balsam yields (Dieterich<sup>5</sup>) about 5% of a thick yellowish oil having an odour like that of the original material. In this way volatile adulterants can be detected. For the oil from the genuine balsam Sortell<sup>6</sup> describes the following characters: sp. gr. 1.0869 at 17°, saponification values 245.7,  $[\alpha]_D + 1.876^\circ$ . After saponification the oil had sp. gr. 1.002 and  $[\alpha]_D + 4^\circ$  at 20°, and it was found to contain benzyl alcohol and peruvial, the greater part of which distilled at 98°/16 mm. Benzoic and cinnamic acids were products of the hydrolysis.

<sup>1</sup> *Caesar and Lorets Jahres-Ber.*, 1912, 20.

<sup>2</sup> *Pharm., J.*, 90, 210.

<sup>3</sup> *Apoth. Zeit.*, 1911, 26, 283.

<sup>4</sup> *Ber. deuts. Pharm. Ges.*, 1913, 23, 622.

<sup>5</sup> *Ber. deuts. Pharm. Ges.*, 1914, 24, 225.

<sup>6</sup> *Ber. deuts. Pharm. Ges.*, 1914, 24, 233.

Dieterich<sup>1</sup> states that irregularities in the preparation of a genuine balsam may cause abnormal colourations in the nitric acid and zone tests.

### Tolu Balsam.

The following description of Tolu balsam is given in the British Pharmacopœia, 1914.

“Soluble in alcohol (90%) the solution being acid to litmus. Acid value 107.4 to 147.2; saponification value 170 to 202. If 5 grm. are gently warmed with three successive quantities of 25, 15, and 10 c.c. of carbon disulphide, the solution yields when evaporated to dryness a distinctly crystalline residue which when tested as described under ‘*Styrax Præparatus*’ yields not less than 1.25 grm. of balsamic acids.”

**Analysis.**—Fleissig states<sup>2</sup> that one of the identity tests of the Swiss Pharmacopœia in which it is directed to treat the substance with alcohol 1:10, should be modified to read specifically 10% ethyl alcohol. Tolu balsam is readily soluble in 95% alcohol. Owing to emulsification there is some difficulty in determining the saponification and acid values. For the latter Merck recommends the following method: 1 grm. of the balsam is dissolved in 50 c.c. of alcohol; 6 c.c. of *N/2* potassium hydroxide solution are added, then a few drops of phenolphthaleïn solution and, after shaking, 200–300 c.c. of water; the excess of alkali is titrated with *N/2* hydrochloric acid. The number of c.c. of alkali solution used up by the balsam  $\times 28$  gives the acid value. The saponification value is determined by dissolving 1 grm. of the balsam in 50 c.c. of alcohol, adding 20 c.c. of *N/2* alcoholic potassium hydroxide and heating for half an hour on a water-bath. Then 200–300 c.c. of water are added and the solution titrated with *N/2* acid. The number of c.c. of alkali consumed in the saponification  $\times 28$  gives the saponification value.

### Liquid Storax.

**Analysis.**—Umney has proposed<sup>3</sup> the following characters and tests as suitable for determining the purity and quality of the natural drug (as distinguished from that impoverished by extraction of valuable constituents with solvents).

*Styrax Purificatus.*—The balsam obtained from the trunk of *Liquidambar orientalis*, purified by solution in alcohol and removal of the solvent.

**Characters and tests.** A brownish-yellow viscous balsam transparent in thin layers, with an agreeable odour and a balsamic taste. Entirely soluble in alcohol and ether. When heated on a water-bath for 1 hour it should not lose more than 5% in weight. When boiled with sulphuric acid and potassium dichromate it evolves an odour of oil of bitter almonds.

<sup>1</sup> *Ber. deuts. Pharm. Ger.*, 1914, 24, 225.

<sup>2</sup> *Schweiz. Wochschr.*, 1911, 47, 365.

<sup>3</sup> *Perf. and Ess. Oil. Rec.*, 1911, 2, 126.

The acid and ester values, when determined in the usual manner, should lie between 60 and 90 and 110 and 140, respectively. To estimate the total cinnamic acid, the alcohol is evaporated from the saponified solution and the residue dissolved in 50 c.c. of water. The solution is transferred to a separator, washed with 10 c.c. of ether and the ethereal layer rejected. The aqueous liquid is acidified with *N*-sulphuric acid and the liberated acids extracted with ether. The ethereal solution is evaporated and the residue extracted with 100 c.c. of boiling water. The extract is filtered whilst hot, the filtrate cooled to 15° and the crystals deposited collected on a tared filter paper. The extraction of the residue is repeated twice with the filtrate heated to boiling and the crystals collected on the same filter. The latter is dried at 100° and weighed. To correct for the solubility of cinnamic acid 0.030 gm. must be added to the weight obtained. The latter should be at least 0.375 gm. from 2.5 gm. of storax.

In criticism of Umney's process, Hill and Cocking state<sup>1</sup> that cinnamic acid cannot be completely extracted from the mixed organic acids by shaking three or even five times with hot water, and that it cannot be dried to constant weight at 100°. It is preferable to boil the mixed organic acids with water under a reflux condenser, and to dry the acid *in vacuo* over sulphuric acid or to dissolve it in alcohol and titrate with standard alkali.

According to Ahrens,<sup>2</sup> genuine *Styrax liquidus* has the following characters: The substance is mixed with sand and ground with light petroleum. The extract is collected, the solvent distilled off and the residue weighed. The amount soluble in light petroleum varies from 37.6 to 56%, average 45.2%. The acid value of the extract varies from 33.1 to 62.9, average 46.7, the cold saponification value 191.3 to 201.3, average 196.1. The iodine value of the extract should be determined if the presence of olive oil or castor oil is suspected.

The British Pharmacopœia, 1914, gives the following description of *Styrax Præparatus*.

"Prepared storax is a viscid balsam obtained from the wounded trunk of *Liquidambar orientalis*, *Mill.*, purified by solution in alcohol, filtration and evaporation of the solvent.

"Entirely soluble in alcohol (90%) and in ether. Boiled with a solution of potassium chromate and sulphuric acid it evolves an odour of benzaldehyde. Loses not more than 5% of its weight when heated in a thin layer on a water-bath for 1 hour. Acid value not less than 60 or more than 90; ester value not less than 100 or more than 146. Yields not less than 20% by weight of cinnamic acid when tested by the following process

"Dissolve 2.5 gm. of the storax in 25 c.c. of *N*/2 alcoholic solution of potassium hydroxide, boil for 1 hour under a reflux condenser, neutralise with *N*/2 solution of sulphuric acid, remove the alcohol by evaporation, and dissolve the residue in 50 c.c. of water. Shake this aqueous solution with 20 c.c. of ether; after separation remove the ethereal layer, wash it with 5 c.c. of water and add the washings to the aqueous solution, rejecting the ethereal liquid. Acidify the aqueous solution with diluted sulphuric acid and shake it with four

<sup>1</sup> *Chem. and Drug.*, 1912, 52.

<sup>2</sup> *Z. offenl. Chem.*, 1912, 18, 267.

successive portions each of 20 c.c. of ether. Mix the ethereal solutions, wash with a few c.c. of water, transfer to a flask and distil off the ether. To the residue add 100 c.c. of water and boil vigorously for 15 minutes under a reflux condenser. Filter the solution while hot, cool to 15.5°, and collect on a tared filter the crystals of cinnamic acid that have separated. Repeat the extraction of the residue with the filtrate at least three times or until no more cinnamic acid is removed. Press the filter paper and crystals between blotting paper, dry in a desiccator over sulphuric acid and weigh. Add to the weight of the crystals so ascertained 0.03 gm. (representing the average amount of cinnamic acid remaining dissolved in the aqueous liquid). The total weight is not less than 0.5 gm."

## SALICYLIC ACID AND ITS ALLIES.

### Commercial Salicylic Acid.

The British Pharmacopœia, 1914, gives the following standard of purity for salicylic acid:

"Shaken with a small proportion of water, the mixture filtered and the solution evaporated, there remains a white residue, having no buff-tinted fringe (absence of iron, organic impurities, and colouring matter). When 1 gm. of the acid is dissolved in excess of a cold solution of sodium carbonate, the liquid shaken with an equal volume of ether, and the ethereal solution allowed to evaporate spontaneously, the residue, if any, is free from the odour of phenol (absence of phenol). Arsenic limit, 2 parts per million. No appreciable ash."

**Reactions and Detection.**—A number of new reactions of salicylic acid have been described. Three of those given by Reichard<sup>1</sup> are as follows: If a little salicylic acid be added to a small quantity of titanous acid, which has been moistened with sulphuric acid and heated for a short time, the mixture set aside for a few hours and then treated with a drop of aqueous potassium hydroxide solution, a fine orange-red colouration is produced. A mixture of salicylic acid and copper sulphate moistened with hydrochloric acid loses its green colour when exposed to the air, but after some days a reddish-violet colouration appears, resembling the biuret indication. When mixed with salicylic acid a concentrated solution of potassium ferricyanide turns dark green. This becomes bluish black on addition of a drop of strong aqueous potassium hydroxide solution, but the colour disappears on shaking, leaving the liquid a slightly green brownish yellow.

Self has described<sup>2</sup> a new colour test for salicylic acid. The substance to be tested is moistened with a cold mixture of equal volumes of concentrated sulphuric acid and 40% formaldehyde and then stirred with a little ammonium vanadate. For 1 mg. of salicylic acid about 2 drops of the liquid and 2–3 mg. of vanadate should be used. In the presence of salicylic acid a Prussian blue colour is produced immediately on adding the vanadate. The test is given by as little as 0.02 mg. of the acid; salicylaldehyde and

<sup>1</sup> *Pharm Zentrh.*, 1910, 51, 743.

<sup>2</sup> *Pharm J.*, 1915, 94, 521.

methyl salicylate also respond to it. All other phenolic substances either give no colouration (except that of the reagents alone, an orange colouration changing to green) or give various shades of red, brown or green, usually changing to brown.

According to Wilkie<sup>1</sup> a perceptible precipitate of 2:4:6 tri-iodophenol is produced when equal volumes of *N*/10 iodine solution and *N*/10 sodium carbonate solution, followed after 5 minutes by excess of sulphuric acid, are added to a solution of sodium salicylate containing as little as 1 part of salicylic acid in 870,000.

McCrae states<sup>2</sup> that Kobert's reagent—3 drops of formaldehyde solution in 3 c.c. of sulphuric acid—gives a characteristic rose colouration with salicylic acid.

Barral describes<sup>3</sup> four additional tests for salicylic acid. If 2 drops of a 5% solution of a salicylate are mixed in a test-tube with 2 c.c. of sulphuric acid and 10% sodium nitrite solution added drop by drop with continuous agitation, the liquid becomes in succession orange yellow, reddish orange, blood red with a greenish tinge, gooseberry red. On adding water it changes to orange coloured. When 2–3 c.c. of a 1% salicylic acid solution are warmed with a fragment of ammonium persulphate the size of a pea, the liquid becomes yellow, then brown and finally gives a brownish-black precipitate. On prolonged boiling the liquid becomes colourless. 3 or 4 drops of a dilute salicylic acid solution dissolved in 1–2 c.c. of sulphuric acid give a stable indigo-blue colour with 2 or 3 drops of Mandelin's reagent. With salicylic acid Schlagdenhaufen's reagent in the cold gives a yellow colouration, which deepens to orange and orange brown on warming, with formation of a red precipitate of selenium and evolution of hydrogen selenide. The first, second and fourth of these reactions are given by salicylic esters, the fourth by sulphosalicylic acid and by aspirin.

According to Sherman and Gross<sup>4</sup> Jorissen's test, when carried out in the following manner, is considerably more delicate than that using ferric chloride. The solution to be tested is treated with 4–5 drops of a 10% solution of sodium or potassium nitrite, 4–5 drops of a 50% solution of acetic acid and 1 drop of a 1% solution of copper sulphate, the liquid being shaken after the addition of each reagent. After heating in a boiling water-bath for 45 minutes and cooling, the colour is examined against a white background, a blank test being carried out in a similar manner. In this way 0.000005 to 0.00001 grm. of salicylic acid in aqueous solution can be detected; faint but perceptible indications are obtained with 5–8 c.c. of a 1:1,000,000 solution and with 18–25 c.c. of a 1:3,500,000 solution. Benzoic, cinnamic and tartaric acids, maltol, isomaltol, orcinol, arbutin, resorcinol

<sup>1</sup> *J. Soc. Chem. Ind.*, 1911, 30, 402.

<sup>2</sup> *Analyst*, 1911, 36, 540.

<sup>3</sup> *Bull. Soc. Chim.*, 1912 [iv], 11, 417.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1911, 3, 492.



and phloridzin do not respond to the Jorissen test. A 1 : 100,000 solution of phenol gives the same colour as a 1 : 1,000,000 solution of salicylic acid. Saligenin gives a red colour at the dilution 1 : 10,000, yellowish tint at 1 : 100,000 but no reaction at 1 : 1,000,000.

During the last four years a number of authors have published methods of detecting salicylic acid in foods and beverages, but for the most part these only differ from those previously known in minor details, e.g., in the variation of the immiscible solvent used.

Thus Stoecklin for the rapid detection in wine and beer recommends<sup>1</sup> the use of dichloroethylene. This author also prefers the Jorissen test in the case of beer and bread.

von der Heide and Jakob<sup>2</sup> extract wine with chloroform. For the detection in milk Philippe<sup>3</sup> (see also Thomann<sup>4</sup>) coagulates with Fehling solution and after acidifying with hydrochloric acid, extracts with ether. Cattini<sup>5</sup> extracts with toluene.

**Estimation.**—A biochemical method of estimating small quantities of salicylic acid in the presence of excess of *p*-hydroxybenzoic acid has been described by Boeseken and Waterman.<sup>6</sup> These authors state that whilst *p* (and *m*-) -hydroxybenzoic acid can be used by *Penicillium glaucum* as carbon nutriment, the presence of salicylic acid in quantities of more than 1% causes a retardation in the growth of the organism. By comparing the effect on *Penicillium glaucum* of the mixture under investigation with that of standard mixtures of salicylic acid and *p*-hydroxybenzoic acid, they claim to be able to determine quantities of salicylic acid varying from 1 to 10% in an excess of *p*-hydroxybenzoic acid, with an accuracy of about 1%.

**Volumetric Methods.**—Wilkie states<sup>7</sup> that when action between a phenol (e.g., salicylic acid) and iodine is allowed to proceed for 5 minutes only, the product is wholly tri-iodophenol, whilst this substance after 20 minutes is transformed into tetraiododiphenylenequinone. On this he bases the following method of estimating certain phenols. To the dilute sodium salicylate solution (the acid should be neutralised) equal volumes of *N*/10 iodine and *N*/10 sodium carbonate solution are added. After 5 minutes excess of sulphuric acid is added and the residual iodine titrated with *N*/10 sodium thiosulphate solution. A pronounced fading of the brown colour due to the iodine, or in extreme cases the precipitation of 2 : 4 : 6-tri-iodophenol indicates that too little iodine has been added; in such circumstances more iodine and sodium carbonate solution should be introduced and the estimation completed in the usual manner after 5 minutes. The estimation is best effected in stoppered bottles.

<sup>1</sup> *Ann. Falsif.*, 1912, 5, 220.

<sup>2</sup> *Zeitsch. Unter. Nahr. Genussm.*, 1910, 19, 137.

<sup>3</sup> *Mitt. Lebensmittel-unters. Hyg.*, 1911, 2, 377.

<sup>4</sup> *Schweiz. Wochschr.*, 1912, 50, 23.

<sup>5</sup> *Boll. chim. farm.*, 1910, 49, 641.

<sup>6</sup> *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 604.

<sup>7</sup> *J. Soc. Chem. Ind.*, 1911, 30, 398.



von Fellenberg adversely criticises<sup>1</sup> the process of estimating salicylic acid in jams described by Harry and Mummery (Vol. III, p. 485) on the ground that a portion of the salicylic acid volatilises during the distillation of the ether, that the lead precipitate occludes salicylic acid, that all of the latter is not removed by three extractions with ether, and that the salicylic acid is contaminated with fruit acids which interfere with its colourimetric estimation. The author modifies the process as follows: 15 grm. of the sample are mixed with 50 c.c. of warm water, the mixture neutralised with *N*-sodium hydroxide solution and treated with  $(10-a)$  c.c. of sodium citrate solution (prepared by neutralising 35 grm. of the acid with soda and diluting to 500 c.c.),  $a$  being the volume of *N*-sodium hydroxide solution required for the neutralisation. The mixture is now treated successively with 10 c.c. of basic lead acetate solution (sp. gr. 1.24), 10 c.c. of *N*-sodium hydroxide solution, 5 c.c. of *N*-hydrochloric acid and 40 c.c. of saturated sodium chloride solution. The addition of these salts prevents salicylic acid from being retained in the lead precipitate formed. The whole mass is now diluted to 150 c.c., filtered and 100 c.c. of the filtrate acidified with 3 c.c. of 20% hydrochloric acid and extracted with five successive quantities of 50 c.c. of ether. The combined ethereal extracts are made alkaline with 10 c.c. of *N*-sodium hydroxide solution, and the ether removed by distillation. The residual solution is diluted to 50 c.c., acidified with 7 c.c. of 20% hydrochloric acid and treated with a measured excess of *N*/50 bromine solution (prepared by dissolving 0.57 grm. of potassium bromate and 2 grm. of potassium bromide in 1 litre of water). After the lapse of 5 minutes 0.5 c.c. of 10% potassium iodide solution is added for each 10 c.c. of the bromine solution used and the liberated iodine is titrated with *N*/50 thiosulphate solution. Each c.c. of the latter corresponds with 0.00046 grm. of salicylic acid. The bromine and thiosulphate solutions must, in each estimation, be titrated against each other under the same conditions as to dilution, acidity, etc., as in the actual estimation. The difference in the quantities of thiosulphate solution used in the actual estimation and the blank titration gives the amount of salicylic acid present. The author states that the process yields only 90% of the salicylic acid present, and that jams contain substances which combine additively with bromine, the quantity of such substances (calculated as salicylic acid) being about 0.5 grm. per 1000 grm.

Vierhont has described<sup>2</sup> a method of estimating salicylic acid in fruit juices, in which the substance is acidified with sulphuric acid and extracted with light petroleum, alcohol being added to prevent emulsification. This is stated by Heintz and Limprich<sup>3</sup> to be untrustworthy and these authors publish a very similar method but estimate the acid colourimetrically with ferric chloride.

<sup>1</sup> *Zeitsch. Nahr. Genussm.*, 1910, 20, 63.

<sup>2</sup> *Zeitsch. Nahr. Genussm.*, 1911, 21, 664.

<sup>3</sup> *Zeitsch. Nahr. Genussm.*, 1913, 23, 706.

In its turn Heintz and Limprich's process has been declared untrustworthy by Serger.

van Raalte<sup>1</sup> for the estimation of salicylic acid in jams, fruit juices, etc., recommends extraction for 5 hours with dichloroethylene.

**Gravimetric Method.**—Autenrieth and Beuttel state<sup>2</sup> that when phenol, saligenin, salicylic acid or *p*-hydroxybenzoic acid in aqueous solution is treated at ordinary temperature with excess of bromine a quantitative yield of tribromophenol bromide,  $C_6H_2Br_4O$ , is obtained, and the action may be used to estimate any one of these substances (in the absence of the others). A weighed quantity of the substance is dissolved in or emulsified with cold water and shaken thoroughly with excess of bromine-water. After standing for 6 hours or more the precipitate is collected on a weighed filter, washed with a small quantity of dilute bromine-water, dried *in vacuo* over sulphuric acid and weighed.

**Colourimetric Methods.**—According to Linke<sup>3</sup> the colouration given by salicylic acid with ferric chloride is not, as generally assumed, permanent. After 1 hour the violet colouration becomes reddish violet and after 12 hours brownish yellow. But if the solution is stronger than 1 in 50,000 the colour does not change for several days. Linke estimates the free salicylic acid in aspirin tablets by grinding one of these with 25 c.c. of water, adding a drop of ferric chloride solution (the *Liquor Ferri sesquichlorati* of the German Pharmacopœia diluted with 25 volumes of water) and comparing the colour produced with that of standard solutions varying in dilution from 1 in 50,000 to 1 in 200,000.

For the estimation of salicylic acid in marmalades Serger recommends<sup>4</sup> the following process: 20 grm. of the substance are diluted with 30 grm. of water and heated almost to boiling. The liquid is filtered, cooled, and 25 c.c. of the filtrate introduced into a 200 c.c. separating funnel. 5 c.c. of dilute sulphuric acid (1:3) and 100 c.c. of a mixture of light petroleum (3 vols.) and chloroform (2 vols.) are added and the mixture shaken for 3–5 minutes. After settling, 50 c.c. of the chloroform-petroleum layer are filtered into a 100 c.c. cylinder, 1 c.c. of 1% ferric chloride solution is added and the liquid diluted with water to 100 c.c. After shaking for 1 minute the mixture is allowed to separate completely (if separation does not occur quickly 5 c.c. of ether are added and the mixture again shaken), the aqueous layer is diluted to 100 c.c. and its colour matched against that of standards prepared by treating 90 c.c. of water with 1 c.c. of 1% ferric chloride solution and measured volumes of 0.1% salicylic acid solution. The colourations compared should not be more intense than that of an *N*/500 potassium permanganate solution.

<sup>1</sup> *Chem. Weekblad*, 1912, 9, 1004.

<sup>2</sup> *Arch. Pharm.*, 1910, 248, 112.

<sup>3</sup> *Apoth. Zeit.*, 1911, 26, 1083.

<sup>4</sup> *Zeitsch. Nahr. Genussm.*, 1914, 27, 319.

Water which has been shaken with Salol is not affected by T. Sol. of ferric chloride (absence of free salicylic acid and of readily soluble salicylates), and yields no characteristic reactions for sulphates or chlorides. No appreciable ash."

### Derivatives of Salicylic Acid.

**Acetyl-salicylic Acid.**—This is described for the first time in the British Pharmacopœia 1914, which sets the following standard:

"When 0.5 grm. is shaken with 20 c.c. of water and 1 drop of T. Sol. of ferric chloride [5%] is added, no violet colouration is produced (absence of salicylic acid). Lead limit, 10 parts per million. Arsenic limit, 2 parts per million. No appreciable ash."

Linke<sup>1</sup> has utilised the ferric chloride reaction for estimating the amount of free salicylic acid in aspirin tablets (see under Salicylic Acid).

**Estimation.**—For the estimation of acetyl salicylic acid Astruc has described<sup>2</sup> the method originally proposed by the present writer in 1910 (Vol. III, p. 504).

## DIHYDROXYBENZOIC ACIDS AND THEIR ALLIES.

### Vanillin

**Vanilla.**—To detect small quantities of coumarin in factitious vanilla extracts Wichmann has described<sup>3</sup> the following method: 25 c.c. of the extract are made slightly acid with sulphuric acid, 25 c.c. of water added and the whole distilled to dryness. 15–25 drops of potassium hydroxide solution (1 : 1) are added to the distillate which is then rapidly evaporated to 5 c.c. and transferred to a test-tube. The water is now boiled off, and the residue fused to a colourless mass. When cold, the residue is dissolved in a few c.c. of water and made slightly acid with 25% sulphuric acid. The solution is distilled, when the salicylic acid formed from the coumarin during the potash fusion, passes over and may be detected by the addition of neutral ferric chloride solution to the distillate.

Dean<sup>4</sup> modifies Wichmann's method as follows: A de-alcoholised sample of the vanilla extract is treated with 5 c.c. of ammonia and extracted with 15 c.c. of ether; coumarin is dissolved by the ether, but vanillin, salicylic acid and saccharin remain in the aqueous layer. The ether extract is evaporated, the residue treated with 5 drops of 50% potassium hydroxide solution, dried, fused, dissolved in a few c.c. of water acidified with sulphuric acid, and extracted with chloroform. The chloroform solution is tested for salicylic acid, formed from the coumarin, by means of ferric chloride.

The author points out that coumarin would interfere with Durand's test

<sup>1</sup> *Apoth. Zeit.*, 1911, 26, 1083.

<sup>2</sup> *J. Pharm. Chim.*, 1913 [vii], 8, 5.

<sup>3</sup> *U. S. Dept. of Agric., Bureau of Chem.*, Circular No. 95, April 6, 1912.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1915, 7, 519.

for saccharin unless it is removed by extraction with an immiscible solvent in the presence of ammonia.

Winton, Albright and Berry publish<sup>1</sup> analyses of 77 samples of vanilla extract prepared from vanilla beans of different varieties, grades, and lengths by the U. S. P. method. They find that the total acidity ranged from 30 to 52 c.c. of  $N/10$  alkali per 100 c.c.; acidity other than that due to vanillin (by difference), 14–42 c.c. of  $N/10$  alkali; total ash 0.22–0.43 grm. per 100 c.c.; soluble ash 0.18–0.36 grm.; alkalinity of total ash 30–54 c.c.  $N/10$  acid; alkalinity of soluble ash 22–40 c.c.  $N/10$  acid.

**Detection.**—Lecomte has proposed a test for vanillin in quinine wines consisting of mixing an ethereal extract of the wine with dilute hydrochloric acid and adding an alcoholic solution of phloroglucinol; a red zone appears at the junction of the two liquids within about 10 minutes if vanillin is present. Chauvin, however, points out<sup>2</sup> that the reaction is also given by furfural and its derivatives, that these are frequently present in the wines used in the preparation of quinine wines, and that the test is not, therefore, characteristic of vanillin.

**Estimation.**—Hubbard<sup>3</sup> has found the following disadvantages in the official United States method for the colourimetric estimation of vanillin. There is a difficulty in getting the maximum colouration; the original method of adding the ferrous sulphate first gives a deeper colour than the present one where the bromine is added first. It is difficult to add only enough lead cream (lead hydroxide) to decolourise the solution, and when different quantities are added the depth of colour subsequently obtained varies. Dilution of the sample influences the colour. Much larger amounts of ferrous sulphate are necessary in comparison with bromine water to produce a maximum colour. Lead cream forms a yellow crystalline lead vanillin derivative  $(C_8H_7O_3)_2Pb$  which renders a quantitative estimation impossible in the presence of lead.

A new colourimetric method of estimating vanillin has been published by Folin and Denis.<sup>4</sup> 5 c.c. of the flavouring extract are mixed with 75 c.c. of water and 4 c.c. of a solution containing 5% each of basic lead and normal lead acetate, and diluted to 100 c.c. with water. The mixture is rapidly filtered, and 5 c.c. of the filtrate are transferred to a 50 c.c. flask, 5 c.c. of a standard solution of vanillin (1 mg. in 10 c.c.) being placed in another similar flask. 5 c.c. of a phosphotungstic-phosphomolybdic acid reagent are added to each flask and after shaking and allowing to stand for 5 minutes the solutions are made up to 50 c.c. with a saturated solution of sodium carbonate and well mixed. After standing for 10 minutes the solutions are filtered and the colours of the filtrates compared in a Duboscq colourimeter. The reagent is prepared by boiling 100 grm. of pure sodium

<sup>1</sup> *J. Ind. Eng. Chem.*, 1915, 7, 516.

<sup>2</sup> *Ann. Falsif.*, 1914, 7, 420.

<sup>3</sup> *J. Ind. Eng. Chem.*, 1912, 4, 669.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1912, 4, 670.

tungstate and 20 grm. of phosphomolybdic acid (free from nitrates and ammonium salts) with 100 grm. of syrupy (85%) phosphoric acid and 700 c.c. of water for  $1\frac{1}{2}$ –2 hours, cooling, filtering if necessary and diluting to 1 litre. Coumarin, extract of tonka beans and acetanilide do not give the rich blue colour produced by vanillin, and sugar, caramel, and glycerol do not interfere with the test:

In place of the dilute standard vanillin solution given above, Harder<sup>1</sup> recommends a stronger one—2 grm. in 200 c.c. of 90% alcohol—as being more stable.

Doherty<sup>2</sup> expresses the opinion that the most trustworthy method of estimating vanillin in essence of vanilla is to distil the essence, extract the vanillin from the residue with ether, combine with sodium hydrogen sulphite, filter, decompose with sulphuric acid, extract with chloroform, evaporate, dry *in vacuo* and weigh. He also gives the following quick method: 1 c.c. of the vanilla essence is extracted with ether, the extract evaporated over water and the aqueous solution filtered and diluted to 50 c.c. in a Nessler glass. 10 drops of freshly prepared bromine water, and 10 drops of 10% ferrous sulphate solution are then added and the colour matched against that given by a 0.2% vanillin solution under the same conditions.

In a research on extraction by means of immiscible solvents Marden<sup>3</sup> has found that 99.6% of the vanillin can be removed from a vanilla extract, which has been freed from alcohol, by shaking once with 20 c.c. and 3 times with 15 c.c. of ether (all the coumarin and about 93% of the acetanilide are simultaneously extracted). For the removal of the vanillin from the ethereal solution he states that the original method of Hess and Prescott (shaking 50 c.c. with 10 c.c. of 5% ammonia) is the best, as it removes all the vanillin and only 5% of the acetanilide and 3% of the coumarin.

From a study of methods of estimating aldehydes Feinberg<sup>4</sup> concludes that for vanillin the iodine and bisulphite methods each give results amounting to 95.5% of the theoretical, whilst precipitation with *p*-bromophenylhydrazine and *p*-nitrophenylhydrazine give 99% and 100% (approx.) respectively.

According to Lehmann<sup>5</sup> vanillin from clove oil has a different melting point from that from guaiacol. He states that the adulteration of vanillin can be detected and its amount estimated by observations of the sintering point, the melting point as determined in the German Pharmacopœia (*i.e.*, the temperature at which the substance forms a continuous column of liquid containing solid particles) and the point of clear fusion. The more nearly pure the product, the smaller is the difference in temperature between the first sintering and complete liquefaction.

<sup>1</sup> *J. Ind. Eng. Chem.*, 1913, 5, 619.

<sup>2</sup> *J. Roy. Soc., New S. Wales*, 1914, 47, 157.

<sup>3</sup> *J. Ind. Eng. Chem.*, 1914, 6, 315.

<sup>4</sup> 8th Int. Cong. Appl. Chem., 1912, Sect. I, Orig. Comm., 1, 187.

<sup>5</sup> *Chem. Zeit.*, 1914, 38, 388, 402.

## ERRATA IN VOL. III

**Page 408, line 8, for "insolubl" read "insoluble."**

**Page 408, line 2 from bottom, for "oi" read "oil."**

**Page 494, line 14, for "il" read "oil."**

**Page 535, line 10 from bottom, for "phloroglucol" read "phloroglucinol."**

**Page 559, line 3, for "ordinance" read "ordnance."**

**Page 575, line 11, for "20°" read "−20°." Line 12, for "12°" read "−12°." Line 9 from bottom, for "25 to 30°" read "−25 to −30°."**

**Page 593, line 9, for "lime" read "brine."**

**Page 614, line 16 from bottom, for "ordinance" read "ordnance."**

**Page 615, line 14 from bottom, for "boiling" read "heating."**

**Page 616, line 17 from bottom, for "ordinance," read "ordnance."**

# RESINS.

By ERNEST J. PARRY, B. Sc., F. I. C.

**Copal.**—Kahan<sup>1</sup> gives the following characters for Benin copal:

M. p. ....	120° to 166°
Acid value. ....	101.0
Saponification value. ....	149.8
Iodine value. ....	61.0

Willner<sup>2</sup> has examined Loango and Sierra Leone copals and finds them to have the following characters:

	Loango	Sierra Leone
Soluble in ether-alcohol. ....	98.7 %	92.9 %
Acid value. ....	106 to 115	109 to 114
Saponification value. ....	126 to 134	146 to 150

According to Richmond,<sup>3</sup> Manila copal has an acid value of 128 and saponification value 178. He states that it consists essentially of free amorphous acids, a volatile hydrocarbon, an unsaponifiable resin and a body which is probably a lactone. The free acids are stated to have the formula  $C_{10}H_{15}O_2$ ,  $C_{22}H_{34}O_4$  and  $C_{32}H_{50}O_4$ .

A number of copals obtained from British West Africa have been examined recently in the laboratory of the Imperial Institute<sup>4</sup> and the following values recorded.

	Acid value	M. p.
Ashanti. ....	124	180°
Ashanti. ....	134	145°
Ashanti. ....	133	120°
Ashanti. ....	126	128°
Sekondi. ....	133	140°-150°
Sekondi. ....	133	140°-150°
Nigeria. ....	110	180°

**Dammar Resin.**—Coffignier<sup>5</sup> gives the following figures for the best known commercial varieties of dammar resin.

<sup>1</sup> *Arch. Pharm.*, 1910, 248, 443.  
<sup>2</sup> *Arch. Pharm.*, 1910, 248, 265 and 285.  
<sup>3</sup> *Philippine J. Sci.*, 1910, 5, 177.  
<sup>4</sup> *Bull. Imperial Inst.*, 1908, 6, 245.  
<sup>5</sup> *Bull. Soc. Chim.*, 1911, 9, 549.



Variety	Sp. gr. at 18°	M. p.	Acid value	Sap. value	Insoluble in		
					Alcohol	Ether	Acetone
Padang.....	1.036	95°	31.4	33.7	20.3 %	4.5 %	14.7 %
Borneo.....	1.048	120°	35.1	64.5	23.6	9.6	20.4
Singapore.....	1.057	95°	30.1	39.3	19.1	1.0	14.0
Pontianac.....	1.025	110°	19.9	30.9	22.4	4.1	16.4
Sumatra.....	1.004	190°	59.6	64.5	45.5	37.9	45.3
Batjan.....	1.032	105°	18.5	19.6	32.8	3.2	21.3

According to S. Stewart<sup>1</sup> dammar resin may be detected in kauri resin in the following manner. An ethereal or chloroformic solution of kauri resin is not precipitated by alcohol, whereas that of dammar yields a curdy white precipitate. He proposes to extract the sample in a Soxhlet apparatus with absolute alcohol. In the case of kauri resin only vegetable débris and mineral matters are left, but if dammar be present a large amount of chloroform-soluble resin is left undissolved, averaging about 36%. A fair approximation to the amount of dammar present in kauri resin can thus be obtained.

**Dragon's Blood.**—The commercial variety of this resin (*i.e.*, Sumatra Dragon's blood) is the product of *Calamus Draco*, a small palm indigenous to Sumatra.

**Guaiacum.**—E. J. Parry<sup>2</sup> gives the following figures<sup>3</sup> for genuine guaiacum:

Mineral matter.....	% 1-4
Acid value.....	60-70
Soluble in 90% alcohol.....	87-98
Acid value of acetylated resin .....	Not above 50
Ester value of acetylated resin.....	125-150
Methoxyl number.....	70-85
Soluble in petroleum ether.....	Not above 2%

If common rosin be used as an adulterant, the amount is approximately indicated by the solubility in petroleum ether.

Starch is sometimes added as an adulterant, so that all suspected samples should be tested with iodine in the usual manner.

Four samples examined by Evans<sup>4</sup> gave acid values 44.8, 56, 53.2 and 45, or for the alcohol-soluble resins 63, 66, 56 and 65. These samples, however, contained from 9.5 to 29.5% of matter insoluble in alcohol, and are therefore in good agreement with Parry's figures.

Squire<sup>5</sup> gives the following figures for guaiacum.

Acid value of crude lump guaiacum.....	90- 95
Acid value of purified resin.....	90-100
Acid value of natural tears.....	70- 75

The pharmacopœia gives 70-80 as the acid value. Squire's figures do not appear to be confirmed by recent observers.

**Shellac.**—It should be noted that much of the so-called "button lac"

<sup>1</sup> *J. Soc. Chem. Ind.*, 1909, 28, 348.  
<sup>2</sup> *Food and Drugs*, Vol. I, p. 458.  
<sup>3</sup> These figures are for genuine guaiacum freed substantially from extraneous matter and practically represent the alcohol-soluble gums.—E. J. P.  
<sup>4</sup> *Analytical Notes*, 1912, 7, 37.  
<sup>5</sup> *Companion to the British Pharmacopœia*, 18th ed., p. 582.

manufactured in Germany is largely factitious, consisting to a great extent of various other resins, mixed with a small amount of shellac, in imitation of ordinary native manufactured button lac.

In reference to the test devised by E. J. Parry, described on pages 69–70 of Volume IV., the statement that “as little as 15 % of colophony may be detected by this test” should read “as little as 5 %, etc.”

The iodine value of shellac is now universally recognised as the best method for the quantitative estimation of colophony in this product. The Hübl method as recommended by E. J. Parry is accepted as the standard method throughout Europe, whilst in America the Wijs' method is preferred. The latter method generally indicates a higher percentage of rosin than is shown by the Hübl method. In reference to the method of shellac analysis described by Endemann<sup>1</sup> which does not appear to be of much practical value, the author has published some further details, which do not in any way alter the value of the process.<sup>2</sup>

Vaubel<sup>3</sup> prefers the bromine absorption to the iodine value, as a criterion of the amount of rosin present. He determines this value as follows: 5 gm. of finely powdered shellac are shaken in a closed flask with 100 c.c. of chloroform or carbon tetrachloride for about 30 minutes, after which 100 c.c. of water, 20 c.c. of strong hydrochloric acid, and 10 gm. of potassium bromide are added. A solution of potassium bromate (2 %) is then added, 1 c.c. at a time, until the liquid assumes a yellow tint which persists for 30 minutes after the flask has been well shaken. Vaubel states that, determined in this manner, the bromine value of pure shellac is almost 8, whilst that of rosin is 120 to 130.

A useful summary which, however, brings out nothing new, on the analysis of shellac appears in the *J. Soc. Chem. Ind.*, 1911, 30, 780, by Langmuir and White.

**Canada Balsam.**—Canada Balsam contains if pure 70 to 85 % of resin, the remainder being essential oil. The resin contains about 20 % of an indifferent resene, 20 % of amorphous canadinic acid, and 60 % of a mixture of  $\alpha$ - and  $\beta$ -canadolinic acids, with a trace of crystalline canadolic acid.

The Balsam has the following characters:

Sp. gr.....	0.983 to 0.997
Optical rotation.....	+1° to +5°
Ref. index.....	1.5175 to 1.5220
Acid value.....	80 to 90
Ester value.....	4 to 8

The essential oil has the following characters:

B. p.....	160° to 168°
Sp. gr.....	0.862 to 0.865
Optical rotation.....	–26° to –36°
Ref. index.....	1.4720 to 1.4770
Esters (as bornyl acetate).....	Under 1 %

The principal constituent of the essential oil is *l*-pinene.

<sup>1</sup> Vol. IV, p. 72.

<sup>2</sup> *Zeit. angew. Chem.*, 1909, 22, 676.

<sup>3</sup> *Chem. Zeit.*, 1910, 34, 991.

## Copaiba.

**Detection of African Copaiba.**—Cocking<sup>1</sup> has suggested a method of detecting the so-called African copaiba in genuine copaiba balsam. It consists in distilling the balsam *in vacuo* or with steam and afterwards dividing the resulting oil into 10 equal fractions by distillation *in vacuo*, determining the rotation of these fractions. With pure Maranham and Pará balsam oils all the fractions were lævorotatory and showed a very gradual increase in rotation from the first to the tenth fractions. The differences between the rotations of the tenth and the first fractions ("difference value") were invariably negative and ranged in the case of the separate oil from  $-3.7$  to  $-7.6^\circ$ . The rotation of the first fraction was a little below that of the original oil. African copaiba balsam yields an oil of which the separate fractions were dextrorotatory. In this case the rotations show a decidedly higher rate of increase than in the American balsam oil, for which reason the difference value is also much greater, whilst moreover it is positive (about  $+23^\circ$ ). Gurjun balsam oil gave exclusively lævorotatory fractions. The rotation of the first fraction was higher than that of the original oil, after this it decreased with each fraction, so that here also the difference value is positive ( $+44.4^\circ$ ). Between the ninth and the tenth fraction there was a sudden decline. In the writer's opinion this method is useless and the deductions drawn quite unwarranted. Further, the slightest deviation from a given method of distillation will give appreciably different results.

Evans<sup>2</sup> gives the following figures for 18 pure and 11 adulterated samples of copaiba. In all cases the essential oil was distilled *in vacuo*.

## PURE COPAIBAS.

	Balsam values				Essential oil values		
	Acid value	Acid value, non-oily portion	$n_D^{15^\circ}$	Ess. oil, per cent.	Sp. gr.	$n_D^{15^\circ}$	$\alpha_D$
<i>Para</i>							
1	31.1	107.2°	1.5073	71.0	0.904	1.4994	$-30^\circ 30'$
2	30.8	102.6	1.5085	70.0	0.903	1.4993	$-31^\circ 30'$
3	66.5	162.0	1.5094	59.0	0.906	1.4983	$-17^\circ 40'$
4	67.7	118.0	1.5107	42.5	0.895	1.4943	$-29^\circ 0'$
5	42.6	152.0	1.5076	72.0	0.903	1.4999	$-14^\circ 28'$
6	34.0	151.0	1.5107	77.5	0.9065	1.5026	$-18^\circ 45'$
<i>Maracaibo</i>							
7	91.4	170.0	1.5172	46.0	0.902	1.4986	$-8^\circ 20'$
8	80.0	143.0	1.5151	44.0	0.897	1.4971	$-10^\circ 0'$
9	80.2	143.0	1.5136	44.0	0.899	1.4975	$-9^\circ 55'$
10	79.1	143.0	1.5183	44.6	0.903	1.4988	$-9^\circ 5'$
<i>Maranhm</i>							
11	81.3	138.0	1.5137	41.0	0.8985	1.4968	$-17^\circ 52'$
12	86.8	150.0	1.516	42.0	0.9045	1.4992	$-19^\circ 12'$
13	78.2	147.5	1.5135	47.0	0.901	1.497	$-17^\circ 40'$
14	85.4	158.1	1.5152	46.0	0.8985	1.4966	$-21^\circ 41'$
15	84.0	168.0	1.515	50.0	0.903	1.4978	$-16^\circ$
16	89.6	160.0	1.5133	44.0	0.902	1.4977	$-19^\circ$
17	86.8	144.5	1.5137	40.0	0.900	1.4967	$-19^\circ$
18	72.4	120.8	1.5098	44.0	0.8965	1.494	$-20^\circ 30'$

<sup>1</sup> Chem. and Druggist, 1910, 77, 119.

<sup>2</sup> Analytical Notes, 1914, 8, 28.

## ADULTERATED COPAIBAS.

	Balsam values				Essential oil values		
	Acid value	Acid value non-oily portion	$n_D^{15^\circ}$	Ess. oil, per cent.	Sp. gr.	$n_D^{15^\circ}$	$\alpha_D$
<i>Pure</i>							
19	77.1	167.4	1.5100	54.0	0.8905	1.4929	-29° 17'
20	22.4	187.0	1.500	88.0	0.9065	1.499	-9° 0'
21	31.8	156.6	1.5057	79.7	0.9045	1.499	-7° 0'
22	26.0	116.0	1.5048	77.5	0.9025	1.5004	-10° 12'
23	14.5	89.2	1.5023	83.8	0.9085	1.4991	-31° 55'
24	77.3	143.0	1.5117	46.0	0.892	1.4957	-26° 15'
25	80.4	174.0	1.511	54.0	0.8845	1.4934	-34° 15'
<i>Maracaibo</i>							
26	85.2	160.7	1.5128	47.0	0.910	1.4975	-0° 10'
27	87.5	168.3	1.5177	48.0	0.9035	1.4981	-5° 32'
28	78.0	147.0	1.512	47.0	0.903	1.4981	-7° 45'
29	82.2	153.9	1.5176	46.6	0.901	1.4987	-10° 20'

Deussen and Eger<sup>1</sup> have devised a new method for the examination of oil of copaiba, in order to decide whether the balsam is pure or not. The oil specially considered is that of African copaiba. The method is based on the fact that African copaiba oil contains much more cadinene than does Para copaiba oil. The dihydrochloride of cadinene melts at 117°-118°, and that of caryophyllene, the principal sesquiterpene of copaiba oil, at 69°-70°. By fractionating the oil, as indicated below, and preparing the dihydrochloride from the suitable fractions, a comparison of the melting points of the crude products is possible, and this will give marked indications as to the presence or absence of African copaiba. The dihydrochloride is prepared by dissolving the fraction in ether, and saturating with dry hydrogen chloride gas, washing the separated crystals with ether, and drying on a porous plate. The melting points of the dihydrochlorides obtained from pure and from adulterated oil are shown in the appended table:

		Fractions at 9 mm.			
		114°-117°	117°-122°	122°-129°	129°-132°
(1) Pure Para Oil—					
Rotation.....	-8.80°	-11.37°	-12.65°	....	
Yield.....	.....	.....	23%	15%	
M. p.....	.....	.....	75°	76°	
(2) +5% African Oil—					
Rotation.....	-8.88°	-10.25°	-11.33°	....	
Yield.....	.....	.....	25%	{ very small amount	
M. p.....	.....	.....	85°	110°	
(3) +10% African Oil—					
Rotation.....	-6.70°	-7.85°	-7.25°	-4°	
Yield.....	.....	.....	18.5%	10%	
M. p.....	.....	.....	110-112°	115°	
(4) +20% African Oil—					
Rotation.....	-6.20°	-6.45°	-1.94°	+3.66°	
Yield.....	.....	.....	29%	19%	
M. p.....	.....	.....	114-115°	116-117°	

The authors have also shown that caryophyllene yields, when treated with NO<sub>2</sub> in ethereal solution, a crystalline nitro-compound, which they have somewhat unhappily termed nitro-caryophyllene, of the formula

<sup>1</sup> Chem. Zeit., 1912, 561.

$C_{12}H_{19}N_2O_6$ ; it melts at  $159^{\circ}$ – $160^{\circ}$ . The yield of this body obtained from different oils is variable, and will give some indication of the origin of the oil. They give the following results:

	Yield obtained
From caryophyllene from clove oil.....	50–52 %
From Para copaiba oil (1).....	9.5–10 %
(2).....	15 %
(3).....	15 %
(4).....	15–16 %
From Maracaibo oil (1).....	5–6 %
(2).....	3 %
From Maturin oil.....	8–9 %
From Para oil + 10 % gurjun oil.....	13.3–14.3 %
From Para oil + 20 % gurjun oil.....	11.7–12.7 %
From Para oil + 30 % gurjun oil.....	10.7–11.7 %
From Para oil + 50 % gurjun oil.....	7.7–8.3 %

**Gurjun Balsam in Copaiba.**—Gurjun balsam may be detected in copaiba by distilling off the essential oil and dissolving 5 or 6 drops in 10 c.c. of glacial acetic acid mixed with 5 drops of nitric acid. A marked violet-pink colour is developed, its intensity depending on the amount of gurjun oil present. If no colouration results after 2 minutes, any minute colouration occurring afterwards may be neglected, as pure copaiba will occasionally give such a faint indication.

**Characters of Copaiba Oil.**—The following figures are given by Gilde-meister for various types of oil of copaiba (*Die Ätherischen Oele*, 2nd Edition, Vol. II, p. 616).

Balsam	Sp. gr.	Rotn.	Ref. index	Acid value	Ester value
Para.....	0.886–0.910	$-7^{\circ}$ to $-33^{\circ}$	1.493–1.502	0–1.9	0–4
Maracaibo.....	0.900–0.905	$-2^{\circ} 30'$ to $-12^{\circ}$	1.498	0.9–1.0	1–1.6
Bahia.....	0.888–0.909	$-8^{\circ}$ to $-28^{\circ}$	1.494–1.497	0.5–7.9	0–14.9
Maranham.....	0.896–0.905	$-1^{\circ} 30'$ to $-22^{\circ}$	.....	.....	.....
Cartagena.....	0.894–0.910	$-2^{\circ} 30'$ to $-23^{\circ}$	.....	.....	.....
Maturin.....	0.899–0.904	$-7^{\circ} 30'$ to $-10^{\circ} 10'$	1.497–1.500	0–0.6	0.9–3.6
Angostura.....	0.916	$-2^{\circ} 20'$	1.502	10.9	0
Guiana (British)...	0.924	$-9^{\circ}$	.....	.....	.....
Guiana (Dutch)...	0.903–0.906	$-7^{\circ} 30'$ to $-10^{\circ} 30'$	.....	0	6.7
Bolivia.....	0.916	$+18^{\circ}$	1.505	1.1	0.5

**Composition of African Copaiba Oil.**—H. von Soden<sup>1</sup> has examined this oil, the sample in question having a sp. gr. 0.9215, optical rotation  $+21^{\circ}$ , and b. p. from  $266^{\circ}$  to  $270^{\circ}$ . The ester value is about 5–6, and the ester value after acetylation about 10. The principal constituent found was cadinene. Schimmel and Co., however,<sup>2</sup> have shown that this sesquiterpene, although very closely related to cadinene, and yielding cadinene hydrochloride, is not, in fact, identical with cadinene. Traces of  $\beta$ -caryophyllene are also present.

### Ammoniacum.

Genuine samples of ammoniacum, examined by Squire<sup>3</sup> had the following characters:

<sup>1</sup> *Chem. Zeit.*, 1909, 33, 428.

<sup>2</sup> *Report*, April, 1914, 48.

<sup>3</sup> *Squire's Companion*, 18th Edition, page 130.

	1	2	3	4
Ash.....	2.15 %	2.55 %	4.3 %	7.05 %
Acid value.....	106.7	101.04	101.04	101.04
Ester value.....	70.2	64.63	67.44	61.82
Saponification value.....	176.9	165.67	168.48	162.86
Gum.....	23.87 %	21.06 %	18.26 %	9.83 %

Harrison and Self,<sup>1</sup> as the result of the examination of 7 samples give 0.08 to 0.20% as the amount of essential oil present in this gum resin, the ref. index of which varies from 1.4747 to 1.4808.

Asafoetida.

Harrison and Self<sup>2</sup> give a number of figures covering their examination of certain samples of asafoetida, and suggest that 1.5% of sulphur in the essential oil, expressed as a percentage of the actual gum resin present might be accepted as a minimum figure. These samples gave the following results:

Nature	Loss on drying, %	Re-sin, %	Ash, %	Oil, %	Oil as per-centage of gum resin	Sp. gr. of oil	Ref. index of oil at 20°	Rotation of oil (1 dcm.)	Percent-age of sulphur in oil	Sulphur in oil as percent-age of drug	Sulphur in oil as percent-age of gum resin
Mixed, chiefly soft paste.	22.3	50.1	4.3	17.7	18.5	0.929	1.5014	— 0° 11'	22.3	3.95	4.13
Soft paste.....	26.0	41.3	3.6	8.3	8.3	0.943	1.5083	— 10° 20'	27.3	2.27	2.35
Soft paste.....	32.2	52.1	3.9	19.6	20.4	0.919	1.4968	+ 4° 13'	17.3	3.37	3.53
Stiff paste.....	24.4	23.9	43.7	5.5	9.8	0.964	1.5124	— 9° 2'	21.7	1.19	2.13
Soft mass.....	18.7	20.9	52.6	5.9	12.4	0.973	1.5130	— 11° 43'	20.7	1.22	2.57
Soft conglomerate...	24.0	56.8	2.7	13.9	14.3	0.973	1.5154	— 9° 20'	23.6	3.28	3.37
Dry conglomerate...	18.8	54.1	6.2	11.1	11.8	0.918	1.4951	+ 10° 58'	17.1	1.90	2.02
Hard mass, or "rock"	7.9	19.4	46.1	4.6	8.5	0.993	1.5259	— 8° 23'	31.4	1.44	2.67
Large tears.....	18.4	50.5	12.4	6.8	7.8	0.959	1.5089	— 10° 23'	21.1	1.43	1.65
Tears.....	.....	.....	.....	17.1	.....	.....	1.5078	.....	17.5	2.99	.....
Tears.....	.....	.....	.....	20.8	.....	.....	1.5037	.....	8.9	1.85	.....

Sechler and Becker<sup>3</sup> give the following method of detecting ammoniacum and galbanum in asafoetida.

If 2 c.c. of a 1 in 10 aqueous emulsion of asafoetida diluted with 5 c.c. of water is floated on sodium hypobromite solution, an olive-green colour results. Galbanum emulsion gives a similar colour; but ammoniacum gives a cherry-red tint. Ammoniacum mixed with asafoetida gives a transient red colour. The reagent is prepared from sodium hydroxide, 20 grm.; bromine, 5 c.c.; water to 100 c.c. If 2 c.c. of asafoetida emulsion be floated on cold sulphuric acid no perceptible change occurs. Ammoniacum also gives no marked reaction. Galbanum gives a violet colour. On distilling off the essential oil, marked differences in appearance are noted. Oil of asafoetida is colourless and has a refractive index = 1.4974. The

<sup>1</sup> Year Book of Pharmacy, 1912, 431.  
<sup>2</sup> Year Book of Pharmacy, 1912, 420.  
<sup>3</sup> Amer. Jour. Pharm., 1912, 84, 4.

gum resin yields about 4% of oil. Ammoniacum only yields 0.2% of dark yellow volatile oil which distils with difficulty; its ref. index is 1.4765. Galbanum yields 20% of light yellow oil with the ref. index 1.4840. Consequently the presence of colour in the oil distilled from asafoetida should be regarded as suspicious. The ref. index should not fall below 1.496. The ref. index of a mixture of asafoetida and ammoniacum was 1.4959, that from asafoetida and galbanum 1.4929.

In most cases, however, the ref. index of oil of asafoetida exceeds 1.5000.

The United States Customs Authorities recently laid down a limit for the "lead number" of genuine asafoetida. The method of determining this figure is as follows:

Sufficient of the sample (about 20 grm.) is taken to furnish between 5 and 10 grm. of the resin. The alcohol-insoluble material is determined in the usual manner. The first two filtrates, representing the major part of the sample, are transferred to a casserole, and the alcohol evaporated on the steam-bath. The resin is then dissolved in ether, filtered, transferred to a separator, and washed with water until the aqueous layer separates clear without any milkiness. The ether solution is filtered through a dry paper into a flask or beaker, and the solvent evaporated on the steam-bath.

Into a small tared beaker weigh roughly about 1.1 to 1.2 grm. of the resin prepared as above, and dry in the air-bath at 110° C. for 5 hours. Place in a desiccator, cool, and weigh. Dissolve in 20 c.c. of 95% alcohol, boiling gently until the resin is in solution. Transfer to a graduated 100 c.c. flask, washing the beaker with hot 95% alcohol, care being taken that the final volume does not exceed 70 c.c. Add 25 c.c. of the alcoholic lead acetate solution (described below), and allow to stand over night. Make up to the mark, filter through a fluted paper, and pipette into a beaker an aliquot of 25 c.c., add 10 c.c. of water, and evaporate to 10 c.c.; add 5 c.c. of 10% sulphuric acid, and then 100 c.c. of alcohol, stirring vigorously to dissolve any separated resin. Filter off the lead sulphate on a tared Gooch crucible, and determine the lead in the usual way.

Carry out a blank on the alcoholic lead acetate solution, and calculate the amount of lead absorbed by 1 grm. of the dried resin. The number of milligrams of lead per gram is the lead number.

A good asafoetida should, according to the above authorities, have a lead number of at least 200.

The alcoholic lead acetate solution is thus prepared:

Dissolve 5 grm. of lead acetate in 20 c.c. of water, and add 80 c.c. of 95% alcohol. A turbidity generally results due to the precipitation of lead carbonate caused by the carbon dioxide contained in the alcohol. Allow to stand over night. The clear supernatant liquid can then be used without filtration for the determination of the lead number.

It will be seen that the "lead number" is thus a measure of the con-



stituent (or constituents) of the ether-soluble portion of the resin which form a lead compound insoluble in alcohol.

The writer,<sup>1</sup> however, showed that this test is misleading and valueless. Rippetoe<sup>2</sup> and Harrison and Self<sup>3</sup> have confirmed the writer's conclusions that this test is worthless.

### Elemi.

Manila elemi contains up to 30% of an essential oil containing much terpenes and having a sp. gr. varying between 0.875 and 0.910, and is dextrorotatory, to the extent of about  $+30^{\circ}$  to  $+40^{\circ}$ . It has a ref. index about 1.4850.

African elemi<sup>4</sup> is derived from other canarium species and three samples examined had the following characters:

	1	2	3
Ash.....	0.6%	0.53%	0.3%
Acid No.....	55.3	37.8	29.4
Sap. No.....	71.9	46.2	44.8
Oil, %.....	8.1	4.4	11.2
Sp. gr. of oil.....	0.8686	.....	0.8451
$[\alpha]_D$ of oil.....	$+50.5^{\circ}$	.....	$+79.3^{\circ}$

### Galbanum.

Good samples of galbanum should not yield more than 10% of ash, which is the limit fixed by the German Pharmacopœia.

The essential oil of galbanum varies considerably according to the age and species of the gum. Samples examined by the writer had sp. gr. between 0.910 and 0.940 and optical rotations from  $-5^{\circ}$  to  $+30^{\circ}$ . The identified constituents are pinene and cadinene.

Harrison and Self<sup>5</sup> examined two samples which had the following characters:

	Sp. gr.	Ref. index	Opt. rotn.
1.....	0.908	1.4856	$+15^{\circ} 14'$
2.....	0.955	1.4869	$+7^{\circ} 30'$

### Myrrh.

Myrrh, according to von Friedrichs<sup>6</sup> contains 3 resin acids soluble in ether,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -commiphoric acids. The first 2 are isomeric, having the formula  $C_{14}H_{18}O_4$ , whilst  $\gamma$ -commiphoric acid has the formula  $C_{17}H_{22}O_4$ .

<sup>1</sup> Chem. and Druggist, 1913, 82, 34.

<sup>2</sup> Amer. Jour. Pharm., 1913, 85, 199.

<sup>3</sup> Pharm. Jour., 1913, [4] 36, 218.

<sup>4</sup> Bull. Imperial Instit., 1908, 6, 252.

<sup>5</sup> Year Book of Pharmacy, 1912, 430.

<sup>6</sup> Arch. Pharm., 1909, 245, 427.

A resin ester of commiphorinic acid  $C_{23}H_{36}O_8$  is also present. Two phenolic substances were also isolated,  $\alpha$ -herabomyrrhol  $C_{18}H_{26}O_5$ , and  $\beta$ -herabomyrrhol  $C_{20}H_{26}O_6$ . A volatile alcohol,  $C_{14}H_{22}O_2$  exists in small quantity, and *heraboresene*,  $C_{42}H_{56}O_8$  is present. Two resin acids insoluble in ether have been termed  $\alpha$ -myrrholic acid,  $C_{15}H_{22}O_7$  and  $\beta$ -myrrholic acid  $C_{25}H_{32}O_6$ . The gum present in myrrh is dextrorotatory,  $[\alpha]_D = +23.8^\circ$ .

Genuine myrrh should not yield more than 8% of ash, picked samples giving only 3.5 to 6%. Six pure samples examined by the writer had the following characters:

	1	2	3	4	5	6
1. Sol. in 90% alcohol, %.....	33.8	41.9	38	37.5	36	43
2. Sol. in water, %.....	29.5	31.2	37	40.5	38.5	34
3. Sol. in petroleum ether, %.....	19.6	20.1	17.5	18.5	20.8	16.5
Acid value of 1.....	59	68	66	70	72	66.4
Ester value of 1.....	108	121	117	131	119	124
Acid value of sample.....	20.5	27	26	28	23	20.5
Ester value of sample.....	34	48	45	50	43	50

**Oil of Myrrh.**—The essential oil of myrrh described in Vol. IV, (p. 103) is not typical and was probably impure. Normal oil of myrrh has a sp. gr. 0.985 to 1.046 and is lævorotatory up to  $-90^\circ$ . Its ref. index is about 1.5360, acid value 5 to 10, and ester value about 45 to 50. Pinene, limonene and dipentene are present, as well as two sesquiterpenes. Eugenol *meta*-cresol and cumic aldehyde are present in traces.

Two pure samples of Somaliland myrrh (*Ogo malmal* and *Guban malmal*) have been examined in the laboratories of the Imperial Institute.<sup>1</sup> The results obtained are compared in the following table with those from commercial Aden and Somali myrrhs.

	Myrrh I. Ogo malmal	Myrrh II. Guban malmal	Commercial myrrh, Aden type	Commercial myrrh, Somali type
	%	%	%	%
Moisture.....	10.2	10.5	8.9	12.9
Ash.....	3.0	5.2	18.0	4.4
Volatile oil.....	13.8	11.8	(not determined).	
Resin, soluble in alcohol.....	31.7	29.7	31.0	22.3
Matter insoluble in alcohol.....	54.5	58.5	60.1	64.8
Consisting of:				
Matter soluble in water (gum)....	52.1	56.8	36.2	58.6
Matter insoluble in water (chiefly dirt).	2.4	1.7	23.9	6.2
Acid value.....	26.5	17.8	19.0	40.5
Saponification value.....	143.0	130.0	97.0	120.0

ERRATA IN VOL. IV.

Page 6, line 8, delete “abietic” (compare page 23).

Page 69, bottom line, “15%” should read “5%.”

Page 96, Manila Elemi apparently is derived from *Canarium Euzonicum* (*Bull. Imp. Inst.*, 1908, 6, 252).

<sup>1</sup> *Bull. Imp. Instit.*, 1914, 12, 11.

# INDIA-RUBBER, RUBBER SUBSTITUTES AND GUTTA-PERCHA.

By E. W. LEWIS, A. C. G. I.

## INDIA-RUBBER.

Although much work has been published on the subject of rubber analysis during the last 3 or 4 years, it cannot be said that any great advance has been made beyond the position recorded in the fourth volume of this work.

**India-rubber Latex.**—With the analysis of *Funtumia elastica* latex, quoted in Vol. IV, p. 106, may be compared that published by Fickendey,<sup>1</sup> of a sample considered by Schidrowitz<sup>2</sup> to be more normal, and those of two Malay *Hevea* latices,<sup>3</sup> a *Ficus elastica* latex,<sup>4</sup> and a *Castilloa elastica* latex,<sup>4</sup> published by Beadle and Stevens.

	<i>Funtumia</i>	<i>Hevea</i> , 4-year old	<i>Hevea</i> , 10- year old	<i>Ficus</i> <i>elastica</i>	<i>Castilloa</i> <i>elastica</i>
	%	%	%	%	%
Water.....	47.68	70.00	60.00	59.5	62.7
India-rubber.....	40.72	27.07	35.62	37.3	31.2
Resins.....	4.46	1.22	1.65	.....	.....
Protein.....	.....	1.47	2.03	0.4	0.2
Mineral matter.....	0.99 <sup>5</sup>	0.24	0.70	0.4	0.9
Lead acetate ppt.....	1.98	.....	.....	.....	.....
Peptones.....	3.25	.....	.....	.....	.....

Chlorogenic and saccharic acids have been found in the latices of *Castilloa elastica* and *Ficus elastica*.<sup>6</sup>

**India-rubber.**—The presence of *l*-methylinositol in raw Para rubber has been referred to by Pickles and Whitfeild.<sup>7</sup> This substance may appear in the acetone extract of the crude (unwashed) rubber to the extent of 2 to 3%.

**Resins.**—The optical activity of the resins accompanying india-rubber from various botanical sources<sup>8</sup> has been confirmed as the result of further work by Hinrichsen and his collaborators.<sup>9</sup> All the resins examined, of which

<sup>1</sup> *Tropenpflanzer*, 1909, No. 5. Gummi-Zeit., 1909, 24, 12.

<sup>2</sup> "Rubber," London, 1911, page 123.

<sup>3</sup> *Analyst*, 1911, 36, 6.

<sup>4</sup> Rubber Exhibition "Lectures," London, 1908, page 231.

<sup>5</sup> Mg, Ca, Cl, SO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Al, K, Na.

<sup>6</sup> Gorter, *Rec. Trav. Chim.*, 1912, 31, 281.

<sup>7</sup> *Proc. Chem. Soc.*, 1911, 27, 54.

<sup>8</sup> Allen's Comm. Org. Analysis, 1911, Vol. IV, p. 125, footnote 3.

<sup>9</sup> *Zeit. angew. Chem.*, 1911, 24, 725.

the botanical origin was definitely known, were found to be optically active, with the exception of those from *Hevea* rubber; the activity is concentrated mainly in the unsaponifiable constituents. The application of these facts to analytical investigations is, however, attended by considerable practical difficulty, and can hardly be attempted, except by a chemist experienced in rubber work, and under favourable circumstances.

**Estimation of India-rubber.**—A reliable method, applicable generally, for the direct estimation of the rubber hydrocarbon, whether in the unvulcanised or in the vulcanised state, is still to seek. In the footnote<sup>1</sup> references are given to a number of papers dealing with the tetrabromide method<sup>2</sup> and its application to unvulcanised and vulcanised rubber. Interesting observations upon some of the obstacles to be overcome in the latter case have been made by Caspari.<sup>3</sup> In the case of unvulcanised (raw) rubber, Budde's method<sup>4</sup> as modified by Spence and Galletly<sup>5</sup> may be usefully employed in some instances.

The sample should first be freed from resins by extraction with acetone. 0.15 to 2.0 grm. of the sample is then cut up into small shreds and soaked for 24 hours in 50 c.c. of carbon tetrachloride. 50 c.c. of a solution of 6 c.c. of bromine and 1 grm. of iodine in 1000 c.c. of carbon tetrachloride are added, and the whole is shaken or stirred at intervals during 6 hours, then vigorously shaken up with 50 c.c. of alcohol and allowed to stand overnight. The liquid is decanted through a filter, the precipitated bromide washed, first with a mixture of carbon tetrachloride and alcohol (2 : 1), then with alcohol, and finally covered with carbon disulphide for 3 to 4 hours. 50 c.c. of benzene (petroleum spirit) are now added, and when the suspended matter has settled the liquid is decanted through the original filter; the sediment is washed thoroughly with alcohol, and dried at a low temperature. The dried bromide is intimately mixed with sodium carbonate and potassium nitrate, in a platinum crucible, covered with more of the mixed carbonate and nitrate, and heated carefully, almost to fusion, for half an hour. The cooled mass is dissolved in water, and the bromine estimated either gravimetrically or by adding excess of *N*/10 silver nitrate to the solution previously acidified with nitric acid, and titrating with standard thiocyanate, using iron alum as in-

<sup>1</sup>Becker, *Gummi-Zeit.*, 1911, 25, 531; 1912, 26, 1503.

Boggs, *Report 8th Int. Congress Appl. Chem.*, 1912, Sect. VB, Orig. Comm., 9, 45-48.

Budde, *Gummi-Zeit.*, 1910, 25, 269.

Each, *Chem. Zeit.*, 1911, 35, 971.

Fendler, *Gummi-Zeit.*, 1910, 25, 311 and 351.

Hinrichsen and others, *Chem. Zeit.*, 1911, 35, 329; 1912, 36, 217.

Hübener, *Chem. Zeit.*, 1910, 34, 1307 and 1315 and 230; 1911, 35, 113. *Gummi-Zeit.*, 1911, 25, 634; 1912, 26, 1711.

Kirchhof, *Gummi-Zeit.*, 1912, 27, 9.

Korneck, *Gummi-Zeit.*, 1910, 25, 4, 42, 77.

Spence, Galletly and Scott, *Gummi-Zeit.*, 1911, 25, 801.

Spence and Galletly, *Gummi Markt*, 1911, 5, 109. *Caoutchouc et Gutta-percha*, 1911, 8, 5313.

Utz, *Gummi-Zeit.*, 1912, 26, 968.

Vaubel, *Gummi-Zeit.*, 1912, 26, 1879.

<sup>2</sup>Vol. IV, p 109-110, 134-136.

<sup>3</sup>*Caoutchouc et Gutta-percha*, 1911, 8, 5289.

<sup>4</sup>*Gummi-Zeit.*, 1909, 24, 4.

<sup>5</sup>*Caoutchouc et Gutta-percha*, 1911, 8, 5313.

indicator. From the amount of combined bromine found the rubber may be calculated by means of the factor 0.425.

**Insoluble Impurities.**—Such impurities in raw rubber as bark, sand, grit, etc. (but not protein) may be estimated<sup>1</sup> by heating 1 gm. of the sample with 5 to 10 c.c. of nitrobenzene, high boiling-point petroleum spirit, or phenotole—preferably the last—for 30 minutes at 100° C., then slowly raising the temperature to 140° C. and maintaining it at this point for 1 to 1½ hours until the gelatinous mass suddenly liquefies. The solution is then poured into 100 c.c. of benzene, the clear liquid decanted, and the insoluble residue washed with benzene by decantation and finally on a weighed filter.

**Nitrogen.**—Of the many variations of the Kjeldahl method Schmitz<sup>2</sup> recommends the following for use with raw rubber: 2 to 3 gm. of the sample are dissolved by heating with 45–50 c.c. of concentrated sulphuric acid in a Kjeldahl flask, with funnel in neck. Frothing may be checked by adding a small piece of paraffin. When cool, 0.25 gm. of cupric oxide and 10 gm. of potassium sulphate are added and the liquid is again heated until it becomes quite clear, and of a greenish colour. Then it is more strongly heated for 1 hour. The total time of heating should not however exceed 4–6 hours. Excess of sodium hydroxide is added and the ammonia is distilled off into excess of standard acid, and titrated iodometrically, using potassium iodate. Ammonium sulphate is recommended for standardisation. The author also advises that the particular variation of the Kjeldahl method employed should always be stated with the result.

**Pyridine Extraction.**—In attempting to estimate the amount of pitchy and bituminous substances present in a sample of vulcanised rubber difficulties are encountered which, in many cases, are still insuperable. The pyridine extract takes no account of any acetone-soluble portions, which constitute a considerable percentage of the various “mineral rubbers” now so largely used, and in their chemical behaviour approximate very closely to other mineral hydrocarbons which may be present in the acetone extract. The difficulty is accentuated by the fact that lightly vulcanised rubber frequently appears in the pyridine extract. In order to minimise the latter difficulty Becker<sup>3</sup> has recommended a carbon disulphide extraction in place of a pyridine extraction. The process is completed much more rapidly and, except in the case of under-cured samples, no appreciable quantity of rubber is dissolved. The fact remains that the carbon disulphide extract constitutes only a portion of the bituminous material present in the original sample, and in this connection the data published by Caspari,<sup>4</sup> showing its distribution as between acetone extract, carbon disulphide extract, and non-extractable organic residue, will be of value, to an experienced rubber analyst, in interpreting the results of an analysis, which can in any case only be approximate.

<sup>1</sup> Beadle and Stevens, *Analyst*, 1912, 37, 13.

<sup>2</sup> *Gummi-Zeit.*, 1912, 26, 1877.

<sup>3</sup> *Gummi-Zeit.*, 1911, 25, 598.

<sup>4</sup> *India-rubber Laboratory Practice*, London, 1914, page 5.

**Mineral Matter.**—The use of anisole or phenetole in dissolving the extracted sample of vulcanised rubber, in order to separate the mineral matter, is recommended by Marcusson and Hinrichsen<sup>1</sup> largely on the ground that the operation can be conducted at so low a temperature that no decomposition occurs of antimony sulphide and other possible ingredients of the mixing. 1 grm. of the acetone-extracted sample is heated with 20 to 30 c.c. of anisole or phenetole in a weighed 100–200 c.c. conical flask at 90–120° C. for 1 to 2 hours. The solution is diluted with benzene, and the mineral matter, separated by means of the centrifugal, is washed in the flask with benzene; after again separating in the centrifugal it is dried at 105° C. and weighed in the flask.

**Estimation of Total Sulphur.**—The use of nitric acid saturated with bromine as the oxidising agent in Henriques' method<sup>2</sup> is found to be advantageous.<sup>3</sup> As the simplest and most reliable method of estimating sulphur in vulcanised rubber, Spence and Young<sup>4</sup> recommend an electrolytic process based on Gasparini's method.<sup>5</sup> 0.5 grm. (or more, according to the rubber content) of the sample is covered with nitric acid (sp. gr. 1.4) in a beaker (100 mm. × 55 mm.) covered by a clock glass. The action is started by gently warming the beaker on a water-bath, and when the rubber is completely dissolved 30 c.c. of fuming nitric acid (sp. gr. 1.5) are poured into the beaker over the lower face of the clock glass. A current of 3 amp. is passed between platinum electrodes, 1 sq. in. in area, immersed in the liquid, with a potential difference of 6–8 volts between them, for 2 to 3 hours in the case of soft rubber, or for 45 minutes to 1 hour in the case of hard rubbers. The electrodes are then removed and washed with water; 1 grm. of sodium carbonate is added to the solution, which is then evaporated to dryness on the water-bath. The residue is freed from nitrates by evaporating with hydrochloric acid, and the sulphur is estimated as barium sulphate.

<sup>1</sup> *Chem. Zeit.*, 1910, 34, 839 (Cf. this Vol., p. 322).

<sup>2</sup> Vol. IV, p. 139.

<sup>3</sup> Waters and Tuttle, *J. Ind. Eng. Chem.*, 1911, 3, 734.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1912, 4, 413.

<sup>5</sup> *Gazzetta.*, 1907, 37 (II), 426.

# ESSENTIAL OILS.

By ERNEST J. PARRY, B. Sc., F. I. C.

## HYDROCARBONS OF ESSENTIAL OILS.

There exist in essential oils a small number of open chain hydrocarbons of the formulæ  $C_{10}H_{16}$  and  $C_{15}H_{24}$ , which are known as aliphatic or olefinic terpenes and sesquiterpenes. Only a few have been isolated, the principal of which are the following:

	B. p.	Sp. gr.	Ref. index	Source
Myrcene, $C_{10}H_{16}$ .....	167°	0.802	1.4673	Bay oil
Ocimene, $C_{10}H_{16}$ .....	73° (21 mm.)	0.801	1.4681	Basil oil.
A sesquiterpene, $C_{15}H_{24}$ ...	270-280°	0.864	1.5185	Citronella oil.

## Terpenes Proper.

**Terpinolene** has been found as a constituent of the oil of Manila Elemi.

**Terpinene.**—Three closely related isomeric terpinenes exist, the formula given on page 171 of Vol. IV, representing  $\alpha$ -terpinene, which closely resembles the  $\beta$ - and  $\gamma$ -varieties.  $\alpha$ -terpinene exists in coriander oil, whilst  $\gamma$ -terpinene is present in ajowan, lemon and coriander oils.

**Phellandrene.**—The following are the characters of the purest forms of phellandrene hitherto prepared.

	B. p.	Sp. gr.	Rotn.	Ref. index
<i>l</i> - $\alpha$ -phellandrene.....	174°	0.848	-84°	1.4769
<i>d</i> - $\alpha$ -phellandrene.....	175°	0.856	+41°	1.4732
$\beta$ -phellandrene.....	57° (11 mm.)	0.850	+15°	1.4759

**Sylvestrene.**—The inactive form of sylvestrene, which has been prepared synthetically by Perkin, is identical with the racemic form of sylvestrene, so that the name *carvestrene* should be replaced by *i*-sylvestrene. It boils at 178°, and yields a dihydrochloride m. p. 52.5° and a dihydrobromide m. p. 48-50°.

**Pinene.**—Two isomeric pinenes are now recognised,  $\alpha$ -pinene and  $\beta$ -pinene (nopinene). Both exist in oil of turpentine, and are very similar in

<sup>1</sup> *Philippine J. Sc.*, 1907, 2, A 17.



properties. The purest forms hitherto produced have the following characters.

	B. p.	Sp. gr.	Rotation	Ref. index	Source
$\alpha$ -pinene.....	155°	0.863	0°	1.4664	Synthetic.
$\alpha$ -pinene.....	156°	0.864	$\pm 48^\circ$	1.4656	Greek turpentine and eucalyptus oil.
$\beta$ -pinene .....	165°	0.865	$-19^\circ 30'$	1.4755	Hyssop oil.
$\beta$ -pinene .....	164°	0.8675	$-22^\circ$	1.4724	Synthetic.

**Fenchene.**—The characters of this terpene are as follows:<sup>1</sup> sp. gr. 0.866 at 15°, rotation  $-32^\circ$ , refractive index 1.4724, and b. p. 156–157°.

Sesquiterpenes

The characters of the principal sesquiterpenes are as follows:

MONOCYCLIC SESQUITERPENES

	B. p.	Sp. gr.	Rotation	Ref. ind.
Bisabolene.....	262°	0.881	$-41^\circ$	1.4901
Zingiberene.....	270°	0.873	$-74^\circ$	1.4940

BICYCLIC SESQUITERPENES

Cadinene.....	272°	0.9205	$-99^\circ$	1.5065
Caryophyllene.....	259°	0.9085	$-8^\circ 40'$	1.5002
Selinene.....	270°	0.923	$+35^\circ$	1.4986
Santalene .....	(See under santal wood oil).			

TRICYCLIC SESQUITERPENES

Cedrene.....	125° (12 mm.)	0.935	$-55^\circ$	1.5023
Clovene.....	262°	0.932	.....	1.5010
Heerabolene.....	135° (16 mm.)	0.945	$-14^\circ$	1.5125

The sesquiterpene humulene has been shown to be an impure form of caryophyllene.

Estimation of Free Acids in Essential Oils.

The estimation of free hydrocyanic acid in essential oils is at times required in the examination of commercial samples. A few years ago, L. W. Andrews<sup>2</sup> described a volumetric method which was based upon the interaction of hydrocyanic acid and mercuric chloride according to the equation  $2\text{HCN} + \text{HgCl}_2 = \text{Hg}(\text{CN})_2 + 2\text{HCl}$ . The free hydrochloric acid generated by the interaction is titrated with *N*/10 potassium hydroxide solution, *p*-nitrophenol being used as the indicator. The difficulty of this method lies in

<sup>1</sup> Wallach, *Annalen*, 1908, 362, 180.  
<sup>2</sup> *Amer. Chem. J.*, 1903, 30, 187.

Andrews' directions that after being diluted with mercuric chloride solution, the liquid has to stand for an hour. Another drawback is the want of clearness in the colour-change of the nitrophenol. According to Rosenthaler<sup>1</sup> the end-point may be more easily observed if iodoeosin is employed as indicator. Rosenthaler also found that the result was equally satisfactory if the action was limited to a short time.

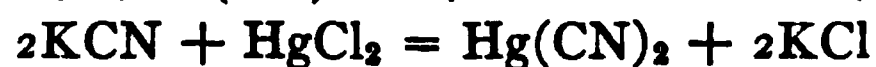
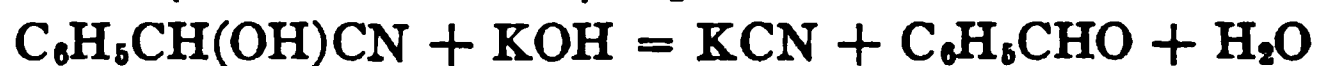
The following are required for the titration:

- (1) *N*/10 potassium hydroxide solution and *N*/10 sulphuric acid.
- (2) Iodoeosin (in 0.2% alcoholic solution) and ether.
- (3) Solution of mercuric chloride.

The estimation is carried out as follows: The liquid under examination, which should contain about 1% of hydrocyanic acid, should be diluted with iodoeosin solution, neutralised with alkali or acid until the solution just shows a pink tinge; mercuric chloride solution is added and the mixture titrated back immediately with alkali, until the colour reappears.

Whether enough mercuric chloride solution has been added is shown by the titrated liquid no longer becoming coloured after the addition of a few drops of this solution. If a colour should appear it is necessary to add more mercuric chloride and to titrate again with potassium hydroxide solution. If there has been overtitration, add an excess of acid and titrate back again. 1 c.c. *N*/10 potash solution = 2.7018 mg. hydrocyanic acid.

The estimation of the total hydrocyanic acid in liquids which contain free hydrocyanic acid and benzaldehydecyanhydrin offers no difficulties. Neutralise with iodoeosin, dilute with excess of *N*/10 potassium hydroxide solution and again shake for 1 minute. Then add acid until decolourisation has been reached and titrate with alkali until the process is completed. In all cases where solutions of unknown strength are concerned, it is advisable, after finishing the titration, once more to add the potassium hydroxide and mercuric chloride solutions, and after allowing the mixture to stand for 5 minutes, to titrate again. The calculation is based upon the following equations:



When free hydrocyanic acid has to be estimated in the presence of benzaldehydecyanhydrin it is not sufficient to dilute the neutralised solution with mercuric chloride and to titrate with alkali, because in that case the results are always too high, inasmuch as the nitrile is decomposed by the alkali as the latter is added. In such a case the best mode of procedure is as follows:

The solution under examination is allowed to run into a separating funnel

<sup>1</sup> *Arch. Pharm.*, 1910, 248, 529.

with about 20 c.c. of saturated neutral sodium sulphate solution and neutralised after adding 50 c.c. of ether and 10 drops of iodoeosin solution. Any sodium sulphate which may be precipitated is re-dissolved by adding water. Mercuric chloride solution is next added, the mixture vigorously shaken, and the aqueous liquid separated into a beaker. The solution remaining in the funnel is then extracted once with 20 c.c. of sodium sulphate solution, and again with only a little of the solution. The extracted acid is titrated in the usual way with alkali.

**Estimation of Phenols.**—One of the most common processes required in the commercial estimation of phenols in essential oils is that of thymol in the oils containing it. According to A. Seidel<sup>1</sup> thymol may be estimated accurately as follows:

Oil containing approximately 0.1 to 0.5 grm. of thymol is placed in a flask of 300 c.c. capacity with 100 c.c. of water. Bromine vapour is then passed into the mixture as long as the brown colour remains permanent after shaking. After standing 20 minutes, 5 c.c. of carbon disulphide and then an excess of a 20% aqueous solution of potassium iodide are added to the liquid. The iodine liberated is titrated with  $N/10$  solution of sodium thiosulphate. Afterwards, an excess of a 2% aqueous solution of potassium iodate is added to the liquid and the free iodine again titrated. The thiosulphate solution required in the second titration corresponds with the thymol present. 1 c.c. of  $N/10$  thiosulphate solution is equal to 0.007506 grm. of thymol.

Redman, Weith and Brock,<sup>2</sup> have lately found that very accurate results in estimating phenols, including thymol, may be obtained by the method proposed by J. M. Wilkie.<sup>3</sup> The method is based upon the same principle as that of Messinger and Vortmann<sup>4</sup> (see Vol. III, pp. 258 and 301), with the exception that sodium hydrogen carbonate is employed instead of sodium hydroxide. The authors recommend the following process. About 50 c.c. of  $N$ -sodium carbonate solution are placed in a glass-stoppered bottle of 500 c.c. capacity and diluted with 100 c.c. of water. 15 c.c. of a solution containing as much of the phenols under examination as corresponds with about an  $N/10$  solution is then added. Iodine solution of about  $N/30$  strength is then added until a permanent brown colour is obtained. The excess of iodine added should be about 20%. The mixture is then vigorously shaken for 1 minute, diluted with 50 c.c. of  $2N$ -sulphuric acid, and the excess of iodine titrated with  $N/10$  thiosulphate solution, 5 c.c. of a 20% solution of potassium iodide being added and starch used as an indicator. In order that the reaction may be rapid and accurate the mixture should be shaken thoroughly after adding the iodine solution. When this is done, the iodine compound is formed within 1 minute. In the case of thymol the compound formed

<sup>1</sup> *Amer. Chem. J.*, 1912, 47, 508.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1913, 5, 831.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1911, 30, 398.

<sup>4</sup> *Ber.*, 1890, 23, 2753.

is thymol di-iodide. In order to make sure that any iodine which may have combined with the hydroxyl group is liberated, care should be taken that a little hydriodic acid is always present, hence the addition of the potassium iodide solution before the excess of iodine is titrated back with thiosulphate. Titration is only to be regarded as complete when the blue colouration distinctly returns even after a lapse of 10 minutes.

### Estimation of Alcohols in Essential Oils.

In practice several difficulties occur in estimating free alcohols in essential oils. It is, of course, understood that in all cases when the alcohols actually exist as a mixture of two or more bodies, the estimation is in fact only a calculation based on the amount of alkali used in saponification, the alcohols being returned in terms of the predominant constituent.

A difficulty occurs in the case of certain alcohols of which linalol may be taken as a type. This alcohol decomposes to a considerable extent under the action of acetic anhydride, so that the results obtained are considerably below the truth. In order to obtain approximately accurate results, Boulez<sup>1</sup> has recommended the following modification of the ordinary acetylation process. 5 grm. of the oil are diluted with 25 grm. of turpentine which has been carefully rectified over sodium, and then boiled with 40 c.c. of acetic anhydride and 3 to 4 grm. of anhydrous sodium acetate. A blank experiment is necessary in order to allow for the apparent alcohol value of the turpentine. This process give results in the case of linalol which are considerably nearer the truth than with the ordinary acetylation process. Xylene gives even better results than turpentine.

It has been recognised by all workers on the subject that the acetylation process, whilst giving excellent results, varies to the extent of several per cent., according to the exact details of the process used. The following details have been therefore agreed upon by most chemists handling essential oils, so that comparative results may be always obtained.

10 c.c. of the oil are boiled under a reflux condenser with 15 c.c. of acetic anhydride and 2 grm. of anhydrous sodium acetate for 2 hours. The mixture is then thoroughly washed with brine until free acid is removed. The washed oil is allowed to stand in contact with anhydrous potassium sulphate for 1 hour with occasional shaking. It is then filtered and a weighed quantity, after exact neutralisation with *N*/10 alcoholic potassium hydroxide, saponified for 1 hour under a reflux condenser with an excess of alcoholic potassium hydroxide; the excess of the last-named should be about equal to the amount necessary for saponifying the acetylated oil.

The following estimations are frequently necessary in practice:

(1) The estimation of actual geraniol in citronella oil, that is, the gera-

<sup>1</sup> *Bull. Soc. Chim.* [iv], 1907, 1, 117.

niol as distinguished from the acetylisable constituents, which include the citronellal.

The following process has been communicated by M. V. Boulez to Messrs. Schimmel & Co.<sup>1</sup> He proceeds as follows: "25 or 50 grm. of oil are shaken in an Erlenmeyer flask with 100 or 200 grm. of sodium hydrogen sulphite solution saturated with normal sulphite, and left standing for 2 or 3 hours until the aldehyde has been completely absorbed. 100 or 200 grm. water are then added and the mixture is heated for several hours under a reflux condenser with frequent shaking, until a complete separation has been effected between the oil layer and the aldehyde compound, which has dissolved in the form of a sulphonic acid. The oil is now isolated in a separating funnel, weighed and acetylated. The loss of oil corresponds with the quantity of citronellal which is present in the oil, and the geraniol content is obtained by acetylating the undissolved oil."

Dupont and Labaune have also published a method for the direct estimation of geraniol in citronella oil.<sup>2</sup>

This process depends on the fact that citronellaloxime, produced by shaking with a cold solution of hydroxylamine, is converted, on heating with acetic anhydride, into the nitrile, which is not affected on hydrolysis with alcoholic potassium hydroxide.

The difference in the molecular weight of the nitrile formed and that of citronellal is so small as to be negligible, and the calculation of the percentage of geraniol from the saponification is made by the usual formula.

The method of procedure is as follows: 10 grm. of hydroxylamine hydrochloride are dissolved in 25 c.c. of water; 10 grm. of potassium carbonate separately dissolved in 25 c.c. of water are added, and the mixture filtered. With this solution 10 grm. of the oil are thoroughly shaken for 2 hours at 15°-18° C. The oil is then separated, dried by means of anhydrous sodium sulphate, and acetylated with twice its volume of acetic anhydride in the usual way for 1 hour on a sand-bath under a reflux condenser. The oil is washed, dried and neutralised and a weighed quantity (about 2 grm.) hydrolysed with alcoholic potassium hydroxide.

(2) The separation of citronellol and geraniol in otto of rose has recently become a matter of considerable importance, as the ratio of the amounts of these alcohols present in genuine otto of rose varies within fairly narrow limits. The addition of geraniol modifies this ratio considerably, hence the value of a process for separating the two alcohols. The process is only approximate and therefore must be carried out under definite conditions. It depends upon the fact that formic acid substantially destroys geraniol, whilst it esterifies citronellol. The total alcohols in the sample are determined by the acetylation process above described, and the citronellol determined by

<sup>1</sup> *Report*, October, 1912, page 44.

<sup>2</sup> *Rouze-Bertrand's Bulletin*, April, 1913, 13.

formylation in the following manner, the amount of citronellol found being deducted from the total alcohols and the geraniol thus calculated.

10 c.c. of the oil are heated for 1 hour on a water-bath in an acetylation flask with twice its volume of formic acid (sp. gr. 1.226). It has been found advisable to add a few pieces of pumice to regulate the boiling. The contents of the flask are cooled and 100 c.c. of water added, and the whole transferred to a separator. The acid layer is run off, and the oil is washed with water until neutral. It is then dried by means of anhydrous sodium sulphate and filtered. The formylated oil is then neutralised and hydrolysed with alcoholic potassium hydroxide in the usual manner, and the percentage of citronellol in the original oil calculated from the following formula:

$$\text{Total citronellol} = \frac{0.156X \times X_{100}}{W - (0.028x)}$$

where  $X$  is the number of c.c. of normal alcoholic potash absorbed and  $W$  the weight of formylated oil.

Umney<sup>1</sup> gives the following typical examples of a number of samples of otto of rose:

	Geraniol by acetylation, %	Citronellol by formylation, %
Bulgarian 1.....	71.1	30.1
Bugarian 2.....	70.1	35.7
Bulgarian 3.....	75.0	36.7
Bulgarian (impure) 4.....	72.6	13.5
Bulgarian (impure) 5.....	70.3	17.0
Bulgarian (impure) 6.....	73.3	22.8
French.....	65.0	33.1
Anatolian imported direct.....	66.7	39.2
Anatolian (via Constantinople).....	73.6	26.2
Persian (m. p. 29-30°).....	38.6	34.5

The last sample, from Persia, is quite abnormal. It has a high melting point and the alcohols contained in it consist very largely of citronellol.

### Esters in Essential Oils.

Although the estimation of esters in essential oils is of extreme value, considerable difficulty in correctly interpreting the results obtained has recently been introduced on account of the abuse of scientific knowledge which has led to the preparation of a series of artificial esters, most of which have a saponification value which would indicate the presence of considerably more natural ester than the actual amount of artificial ester used as an adulterant. The principal esters used in connection with these frauds are as follows: terpinyl acetate, glyceryl acetate, ethyl citrate, ethyl oxalate, ethyl succinate, ethyl tartrate, and ethyl phthalate. Apart from the actual identification of the acid constituents of these esters, the following notes in regard to one or two of them will be of value.

<sup>1</sup> *Perfumery Record*, October, 1913, page 329.



**Terpinyl Acetate.**—This ester is principally found as an adulterant in oil of bergamot, oil of petitgrain, and similar essential oils. The natural ester present in this class of oil consists principally of linalyl acetate. Linalyl acetate is hydrolysed at a considerably more rapid rate than terpinyl acetate. It therefore becomes possible to state with certainty that an artificial ester, probably terpinyl acetate, is present in either of these oils when a marked difference is found between the saponification value as determined at 30 minutes, and that determined in 60 minutes. From the accompanying table<sup>1</sup> it will be seen that hydrolysis of linalyl acetate or of bergamot oil is practically complete in 30 minutes, whereas, the saponification of terpinyl acetate or of bergamot oil adulterated with this ester is much slower.

Ester	Time of saponification, minutes					2 hours
	5	15	30	45	60	
Linalyl acetate (Schimmel & Co.).....	191.5	217.5	223.2	223.7	223.1	224.7
Terpinyl acetate.....	108.2	166.8	209.7	233.4	245.8	262.7
Bergamot oil.....	80.3	94.5	97.3	97.5	97.8	98.5
Bergamot oil + 5 % terpinyl acetate.....	82.5	94.8	101.2	102.1	104.7	107.2
Bergamot oil + 10 % terpinyl acetate.....	79.9	96.4	102.8	105.2	108.3	112.5
Bergamot oil + 25 % terpinyl acetate.....	78.8	100.6	108.1	116.4	119.0	126.8

Small quantities of terpinyl acetate can be detected by a process of fractional hydrolysis. The following process devised by Messrs. Schimmel & Co., yields most accurate results. Three separate saponifications should be made, using about 2 grm. of oil for each test. 5 c.c. of alcohol are then added, and the free acid neutralised with  $N/2$  potassium hydroxide solution. The first saponification should be made for 1 hour with 10 c.c. of  $N/2$  potassium hydroxide; the second should be saponified for 2 hours with 20 c.c.  $N/2$  alkali, and the third for 1 hour with 10 c.c. of  $N/2$  potash and 25 c.c. of 95% alcohol. After saponification the flasks should be cooled quickly by immersion into cold water and titrated at once. In the case of pure oils such as bergamot, petitgrain and lavender, the difference between the saponification for 2 hours and for 1 hour with dilute potassium hydroxide solution will not be more than 3 or 4, whereas, if terpinyl acetate be present, so little as 2% will cause the difference to be from 6 to 7, and 5% will raise it to about 12.

**Ethyl Citrate.**—Essential oils adulterated with ethyl citrate show a marked turbidity at the commencement of the saponification process. This is due to the separation of potassium citrate which is sparingly soluble in alcohol. After boiling for some time, this turbidity may disappear. Pure bergamot or similar oils do not show this turbidity.

The following method of identifying citric acid is due to Denigès:<sup>2</sup> 10 c.c. of the saponification liquor from which the separated oil has been removed, are shaken with 1 grm. of lead peroxide, and 2 c.c. of solution of mercuric

<sup>1</sup> Schimmel & Co.'s Report, Oct. 1910, page 60.

<sup>2</sup> Bull. Soc. Ph. Bordeaux, 1898, 33.



sulphate of about 5% strength. After vigorous shaking the liquid is filtered and 5 c.c. of the filtrate heated to boiling point, and a 2% solution of potassium permanganate added drop by drop, constantly stirring until it ceases to become immediately decolourised. If citric acid is present a flocculent pale yellow or white precipitate develops after the first drop.

**Glyceryl Acetate.**—This adulterant is usually a mixture of glyceryl acetates in which triacetin predominates. Its detection is moderately easy on account of the fact that it is readily soluble in very dilute alcohol, and even fairly soluble in water. Messrs. Schimmel & Co.<sup>1</sup> have proposed the following methods for its detection.

10 c.c. of bergamot oil are mixed in a separating funnel with 10 c.c. of light petroleum and 2.5 c.c. of alcohol, and vigorously shaken up with 20 c.c. of water. The addition of light petroleum and alcohol causes a very rapid separation of the oil and the aqueous liquid, so that the latter can be filtered off when the mixture has been allowed to settle for about 10 minutes. Of the filtrate, 10 c.c. are neutralised with potassium hydroxide and saponified on the water-bath for 1 hour with 5 c.c. *N*/2 potassium hydroxide solution. In the case of pure bergamot oil, the 10 c.c. of filtrate required for saponification.

0.08 c.c. *N*/2 potassium hydroxide solution  
After adding 1% of glyceryl triacetate. 0.58 c.c.  
After adding 2% of glyceryl triacetate. 1.43 c.c.  
After adding 5% of glyceryl triacetate. 2.79 c.c.

= 2.2 mg. KOH  
= 16.2 mg. KOH were used.  
= 40.0 mg. KOH were used.  
= 78.0 mg. KOH were used.

Hence the addition of 1% glyceryl triacetate requires about 15 mg. KOH more for saponification.

Later, Schimmel & Co. proposed omitting the petroleum ether and shaking up 10 c.c. of the oil with 20 c.c. of 5% alcohol. After allowing the 2 layers to separate completely, 10 c.c. of the aqueous layer, which may be filtered, is neutralised, using phenolphthaleïn as indicator, and saponified for 1 hour with 5 c.c. of *N*/2 potassium hydroxide solution. With pure oils not more than 0.1 c.c. of *N*/2 alkali should be required, a higher figure indicating the presence of glyceryl esters. The time taken for the separation of the oil and the aqueous liquids is so long, however, that the use of petroleum ether is preferable. For the positive identification of glyceryl acetate, the same chemists describe the following process.

40 gm. were hydrolysed with the calculated quantity of sodium hydroxide in a concentrated aqueous solution; the solution was then distilled, and, as only water passed over, it was next evaporated to dryness in a dish. The attempt to separate the alcohol (glycerol), which had been split off from the ester, from the sodium salt of the acid by means of an extracting agent failed, because the known solvents took up not only the alcohol but also considerable quantities of the sodium salt. To obviate this difficulty, the sodium salt was decomposed with the calculated quantity of dilute sulphuric acid and the organic acid which was liberated removed by distillation, and subsequently by

<sup>1</sup> *Half-yearly Report*, Oct., 1910, page 61, and April, 1911, page 150.

evaporation. This acid was identified as acetic acid. It was now easy to separate the alcohol of the ester from the residual sodium sulphate by means of ethyl alcohol. When the ethyl alcohol had been evaporated by distilling *in vacuo*, the ester alcohol was identified as glycerol by its b. p.  $147^{\circ}$  (4 mm.).

As Salamon and Seaber<sup>1</sup> have pointed out, glyceryl acetate is so easily washed out with 5% alcohol, that an adulterated oil, when washed several times with alcohol of this strength, will show a distinctly lower ester value than the original unwashed oil. Pure oils of lavender, bergamot and similar oils show practically no reduction in ester value by such treatment.

**Non-volatile Esters.**—When non-volatile or practically non-volatile esters such as ethyl citrate are used for the purpose of adulteration, al-



FIG. 13.—Apparatus for estimation of fixed esters.

most the whole of the esters remain in the residue left on evaporating the oil for from 3 to 4 hours on a water-bath. If the weight of this residue is above the normal for a pure oil, non-volatile esters are strongly indicated and may be approximately determined by estimating the saponification value of the residue itself. The process is carried out as follows: 5 gm. of the oil are evaporated in a platinum dish on a water-bath until the weight is practically constant. The residue is washed into a flask and saponified in the

<sup>1</sup> *Perfumery Record*, 1912, 3, 275.

usual manner. Titration should be effected quickly with phenolphthaleïn as indicator. After the neutral point has been reached, the liquid will acquire a red tint in a short time. No notice need be taken of this as it is due to decomposition of bergaptene or similar bodies. The saponification value of the residue from pure bergamot oil varies from about 135 to 180, usually about 170. The addition of 1% of ethyl citrate will raise it about 50, whilst the addition of 2% will raise it by nearly 100. Messrs. Schimmel & Co. have devised the following method of estimating the amount of fixed esters present as an adulterant in this type of oil. The examination of pure bergamot oil has shown that almost the whole of the acid which is combined with the potassium hydroxide on saponification can be distilled off with steam after acidifying the aqueous solution with sulphuric acid. With pure bergamot oil, therefore, only a little more potassium hydroxide solution is used in ascertaining the saponification number than is required for neutralising the acids which have been distilled off. The estimation is carried out with 1.5 to 2.0 grm. of the oil as follows: the acid and ester numbers are ascertained in the usual manner, and the contents of the saponification flask evaporated to dryness after adding a few drops of  $N/2$  potassium hydroxide solution. The residue is dissolved in about 5 c.c. of water and acidified with 2 c.c. of dilute sulphuric acid. From the flask *A* (shown in the accompanying illustration), fitted with an ascending tube, a powerful current of steam is generated, by which, in about half an hour, 250 c.c. is distilled over into the measuring flask *C* in such a manner that the contents of the saponification flask *B* are kept down to about 10 c.c. with a small flame. Afterwards 100 c.c. more are carried over in the same manner. The distillate, after a few drops of phenolphthaleïn solution have been added, is titrated with  $N/2$  potassium hydroxide solution (or for the sake of accuracy, better still with  $N/10$  solution) until it assumes a red colour. The first 250 c.c. contain very nearly the entire volatile acids, as the next 100 c.c. invariably use up only 0.1 to 0.2 c.c. of  $N/2$  solution. From the quantity of potash solution required to neutralise the entire distillate the acid number (II) is calculated for the weight of the bergamot oil used. The difference between the saponification number of several pure oils which have been examined and the acid number (II) determined in the manner described above, varied (as shown in the table below, Nos. 1-7) from 5.2 to 6.9.

Hence, unless further examination of pure oils should show a higher figure, oils with a greater difference must be regarded as suspect or adulterated.

In the case of the pure esters (Nos. 12 to 14) here examined the difference between the two values was from 596.4 to 745.8. The addition of such esters to oil of bergamot must, therefore, correspondingly increase the difference of both numbers of the adulterated oil (Nos. 15 to 23 of the table).

	Acid No.	Ester No.	Sap. No.	Acid No. II of the oil	Diff.
	of the oil				
No. 1 Bergamot oil.....	1.6	88.7	90.3	84.3	6.0
No. 2 Bergamot oil.....	1.6	90.2	91.8	86.6	5.2
No. 3 Bergamot oil.....	2.0	101.1	103.1	97.0	6.1
No. 4 Bergamot oil.....	2.3	112.3	114.6	107.7	6.9
No. 5 Bergamot oil.....	2.4	100.0	102.4	95.7	6.7
No. 6 Bergamot oil.....	2.3	96.1	98.4	91.8	6.6
No. 7 Bergamot oil.....	2.1	98.3	100.4	95.1	5.3
No. 8 Bergamot oil.....	2.0	98.2	100.2	90.8	9.4
No. 9 Bergamot oil.....	2.0	103.9	105.9	91.8	14.1
No. 10 Bergamot oil.....	2.0	102.4	104.4	87.6	16.8
No. 11 Bergamot oil.....	2.8	103.9	106.7	89.9	16.8
No. 12 Diethyl succinate.....	.....	.....	638.4	7.3	631.1
No. 13 Triethyl citrate.....	0.8	602.6	603.4	7.0	596.4
No. 14 Diethyl oxalate.....	.....	.....	753.0	7.2	745.8
Bergamot oil after adding:					
No. 15 1 % Diethyl succinate.....	2.1	103.5	105.6	94.1	11.5
No. 16 2 % Diethyl succinate.....	2.1	109.9	112.0	93.1	18.9
No. 17 3 % Diethyl succinate.....	2.1	116.2	118.3	92.8	25.5
No. 18 4 % Diethyl succinate.....	2.1	121.7	123.8	91.8	32.0
No. 19 5 % Diethyl succinate.....	2.1	127.6	129.7	91.5	38.2
No. 20 1 % Triethyl citrate.....	2.1	103.4	105.5	94.1	11.4
No. 21 2 % Triethyl citrate.....	2.1	109.1	111.2	92.8	18.4
No. 22 1 % Diethyl oxalate.....	.....	.....	106.6	94.7	11.9
No. 23 2 % Diethyl oxalate.....	.....	.....	113.3	92.5	20.8
No. 24 2 % Glyceryl triacetate.....	2.1	111.2	113.3	108.7	4.6
No. 25 4 % Terpinyl acetate.....	2.4	103.2	105.6	100.0	5.6

Nos. 24 and 25 show that adulteration with the esters of the volatile group cannot be detected by distilling the acids, because in these cases the difference lies of course within the limits for pure oils. The following are average figures for a number of artificial esters.

Ester	Sp. gr.15° C.	Ref. index 20° C.	Ester, %	Range of b. p.
Ethyl formate, pure.....	0.908	1.3621	74.9	54°-65°
Ethyl formate, commercial.....	0.869-0.927	1.360-1.367	59.6- 68.9	55°-80°
Ethyl acetate, pure.....	0.904	1.3740	100.8	75°- 79°
Ethyl acetate, commercial.....	0.901-0.904	1.37371.374	82.8- 94.7	71°- 84°
Ethyl butyrate, pure.....	0.883	1.3922	100.1	110°-120°
Ethyl butyrate, commercial.....	0.883-0.886	1.388-1.492	95.4-100.5	105°-140°
Ethyl succinate.....	1.042-1.054	1.419-1.421	98.0- 99.5	210°-214°
Ethyl sebacate.....	0.959-0.966	1.436-1.439	94.9- 96.4	above 300°
Ethyl benzoate.....	1.048-1.053	1.504-1.545	73.8-100.5	210°-215°
Ethyl cinnamate.....	1.052-1.056	1.557-1.559	99.1-100.6	260°-267°
Ethyl salicylate.....	1.132-1.134	1.521-1.523	96.0- 99.8	225°-230°
Amyl acetate, pure.....	0.860-0.863	1.397-1.402	89.6- 99.6	130°-140°
Amyl acetate, commercial.....	0.863-0.870	1.399-1.402	82.2- 88.9	110°-142°
Amyl butyrate, pure.....	0.867	1.4128	99.9	170°-180°
Amyl butyrate, commercial.....	0.857-0.867	1.407-1.412	76.9- 83.4	135°-180°
Amyl valerate, pure.....	0.858	1.4131	98.7	180°-190°
Amyl valerate, commercial.....	0.850-0.866	1.408-1.413	75.6- 81.8	140°-190°
Amyl salicylate.....	1.048-1.053	1.505-1.508	97.2- 98.7	260°-275°

According to Béhal,<sup>1</sup> the results of the estimation of esters may show differences of between 1 and 3%, especially when formic or acetic esters are in question. He attempts to explain these differences by the suggestion that when esters of high molecular weight are saponified with alcoholic potash, esters of lower molecular weight are first formed, principally ethyl formate and ethyl acetate. Being highly volatile, these are liable to be lost through

<sup>1</sup> Bull. Soc. Chim., 1914, 306.

incomplete condensation; thus benzyl benzoate when heated with alcoholic potash soon develops the odour of ethyl benzoate, and in the same way bis-muth salicylate when treated with potash dissolved in methyl alcohol yields methyl salicylate. He assumes that an intermediate di-ester is formed which then splits off the alcohol of high molecular weight. As a result of these observations, Béhal considers that a number of essential oils contain formic esters in quantities hitherto unsuspected. He considers formic acid constitutes an important part of the esters of Algerian oil of geranium.

### Estimation of Aldehydes and Ketones.

Hanus<sup>1</sup> proposes the following method for the estimation of cinnamic aldehyde, etc. 10 grm. of finely powdered hydrazine sulphate are dissolved in a solution of 9 grm. of sodium hydroxide in 100 cc. of water, and the alkaline sulphate produced is precipitated by the addition of 100 c.c. of alcohol. After filtering, the solution is warmed, 9 grm. of oxamethane are added in small portions, the whole warmed for half an hour and allowed to cool. The azide separates in crystalline tables, and these are separated and recrystallised. To estimate the aldehyde by means of this reagent, a small quantity, not more than 0.2 grm., of the oil is well shaken in 85 c.c. of water, and about 0.35 grm. of semi-oxamazide in 15 c.c. of hot water is added and the whole well shaken. After 5 or 10 minutes the compound begins to be precipitated, and after standing 24 hours can be collected on a Gooch filter, washed with cold water and dried for a few minutes at 105°. The amount of the precipitate is multiplied by 0.6083 to obtain the amount of aldehyde. The constitution of the semi-oxamazone of cinnamic aldehyde is  $\text{NH}_2.\text{CO.CO.NH.N} : \text{CH.CH} : - \text{CH.C}_6\text{H}_5$ .

Feinberg has obtained good results in estimating aldehydes as *p*-nitrophenylhydrazone by the method of W. Alberda van Ekenstein and J. J. Blanksma.<sup>2</sup> In the case of benzaldehyde he proceeds as follows: 25 c.c. of a 1% benzaldehyde solution (in 12% acetic acid) are diluted with 50 c.c. of water and mixed with 30 c.c. of 30% acetic acid containing double the calculated quantity of *p*-nitrophenylhydrazine. After 5 hours the precipitate is collected in a Gooch crucible and washed with 10% acetic acid until a well-defined colouration has ceased to ensue upon the addition of alkali. The precipitate is then dried at 105° to 110° and weighed. The benzaldehyde-content is found by multiplying by 0.44. It is necessary to ascertain by titration the quantity of benzoic acid which is present in the benzaldehyde, and to deduct it from the quantity of benzaldehyde used. The average proportion of benzaldehyde found was about 99%. The same method applies to salicylic aldehyde, but in this case filtration may be commenced after 1 hour (factor 0.4747).

<sup>1</sup> *Pharm. Central.*, 1904, 37.

<sup>2</sup> *Chem. Zentralbl.*, 1905, 1, 1277.

For **vanillin** and **anisic aldehyde** Feinberg gives the following method: Dissolve 0.5 gm. of aldehyde in a little alcohol and acetic acid, and after diluting with 75 c.c. of water and warming, mix the solution drop by drop with constant stirring with a solution of *p*-nitrophenylhydrazine in 2*N*-hydrochloric acid. Filter after 30 minutes in a Gooch crucible and wash with 2*N*-hydrochloric acid and afterwards with water until only a faint opalescence is produced by silver nitrate. For the estimation of the anisic aldehyde use the factor 0.50188; for vanillin, 0.5353.

### Estimation of Citral.

Various colourimetric processes of estimating citral have recently been devised. Of these, the following give fairly accurate and concordant results.

**Hiltner's Method.**—R. S. Hiltner<sup>1</sup> bases a method on the fact that solutions of *m*-phenylenediamine hydrochloride give a yellow colour with solutions of citral, the intensity being dependent on the amount of citral present. This solution, which preferably should be freshly prepared each time, must be quite clear and colourless, and, if necessary, should be made so by treating it with animal charcoal and filtering. The percentage of citral in the extract or oil under examination is determined by comparative tests with a solution of known citral-content (0.25 gm. citral to 250 c.c., dissolved in 50% alcohol).

The test is carried out as follows: 1.5 to 2 gm. lemon oil, or 25 gm. of lemon-extract are diluted to 50 c.c. with 90 to 95% alcohol; 2 c.c. of this solution are poured into the colourimeter-vessel, 10 c.c. *m*-phenylenediamine solution added, and the whole made up to a fixed volume. Comparative tests are made simultaneously in the same manner with the standard solution referred to above, until the precise shade of colour of the solution under examination is reached. The citral-content of the oil or extract of lemon can be calculated from the quantity of the standard solution taken up in the test. If the citral-content is less than 0.1%, it will be desirable to use a little more of the solution under examination, in order to obtain the intensity of colour which is necessary to give exact results.

**Chace's Method.**—Chace<sup>2</sup> has devised a method depending on the property of fuchsine-sulphurous acid of giving a red colouration in the presence of aldehydes. The solution of fuchsine-sulphurous acid is prepared as follows:

0.5 gm. of fuchsine is dissolved in 100 c.c. of water and a solution containing 16 gm. of SO<sub>2</sub> is added and when decolourised the whole is made up to 1,000 c.c. The solution must be freshly prepared, that is, not more than 3 or 4 days old. Alcohol of 95% strength is freed from aldehyde by keeping it in contact with caustic alkali for several days and then distilling, and boiling the

<sup>1</sup> *J. Ind. Eng. Chem.*, 1909, 1, 798.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1906, 28, 1472.

distillate with 25 gm. of *m*-phenylenediamine per litre, for a few hours under a reflux condenser. The alcohol is then finally redistilled. A standard solution of 0.1% of citral in 50% alcohol is prepared. A quantity of the oil or essence containing about 0.1 to 0.2 gm. of citral is diluted to 100 c.c. with 50% aldehyde-free alcohol. 4 c.c. of this solution are used for the determination, and are mixed with 20 c.c. of alcohol and 20 c.c. of fuchsine-sulphurous acid solution, and made up to 50 c.c. with alcohol. After well mixing, the observation tube is kept at about 15° and the colour compared with the necessary standards, from which the amount of citral can be calculated.

**Little's Method.**—Little<sup>1</sup> prefers the following method depending on the use of diaminophenol.

The method is easily manipulated and can be conducted at room temperature:

**Reagent.**—Dissolve 0.2 gm. diaminophenol hydrochloride (commercially known as amidol), in 100 c.c. of 65% by volume alcohol, preferably distilled over potassium hydroxide. The use of aldehyde-free alcohol does not seem to make any difference in the results, as acetaldehyde has no apparent effect upon the reagent. The reagent is very readily soluble in 65% alcohol.

**Standard Citral Solution.**—A solution of pure citral in 50% alcohol, containing 0.001 gm. per c.c.

**Solution of Essence or Extract of Lemon.**—Weigh from 15 to 25 gm. of the extract for examination, and dilute to 30 or 50 c.c. with 50% alcohol, if a terpeneless extract, making a 50% solution.

Place 2 c.c. of the standard citral solution measured from an accurately graduated pipette, in a 250 mm. colourimeter tube, add 20 c.c. of 65% alcohol, and 15 c.c. of diaminophenol reagent and make up to 50 c.c. with 65% alcohol. Place 2 c.c. of the extract in the other tube with 15 c.c. of the reagent and make up to 50 c.c. with 65% alcohol as before, mixing the contents of both tubes thoroughly and allowing both tubes to remain for 5 to 10 minutes at room temperature, when the maximum colour is reached in both the citral tube and the extract under examination. The reading and calculation are made at once or a reading can be made at the expiration of 15 or 20 minutes in duplicate. The calculation of the percentage of citral content in the extract is made by placing the standard citral tube at the 30 mm. mark and adjusting the tube containing the extract under examination so that the 2 small discs of colour as observed through the two immersion tubes are similar in tint.

Kleber<sup>2</sup> uses a method based on the phenylhydrazine reaction, which, as slightly modified by Schimmel & Co., is as follows:

About 2 c.c. of oil are mixed with 10 c.c. of a freshly prepared 2% alcoholic phenylhydrazine solution, and allowed to remain undisturbed during 1 hour

<sup>1</sup> *Amer. Perfumer*, 1914, 74.

<sup>2</sup> *Amer. Perfumer*, 1912, 6, 284.



in a glass-stoppered flask of about 50 c.c. capacity. 20 c.c. of  $N/10$  hydrochloric acid are then added and the liquid is mixed by gently moving the flask backwards and forwards. After adding 10 c.c. of benzene the mixture is shaken vigorously and poured into a separating funnel. The acid layer, amounting to about 30 c.c., which separates clearly after the mixture has been left to settle a short time, is then filtered on a small filter.

To 20 c.c. of this filtrate 10 drops of diethyl-orange solution (1 : 2,000) are added and the mixture is titrated with  $N/10$  potassium hydroxide solution until a distinct yellow colour appears. From this the quantity in c.c. of  $N/10$  potassium hydroxide solution required for 30 c.c. of the filtrate is calculated. For the purpose of estimating the value of the phenylhydrazine solution a blank test without oil is made in a similar manner. If it is found that the quantity of solution used up for 30 c.c. of the filtrate =  $a$  in the first, and =  $b$  in the second experiment, it follows that the quantity of citral present in the amount of oil under test ( $s$  grm.) equals  $a - b$  c.c. of  $N/10$  solution. Hence, 1 c.c.  $N/10$  potassium hydroxide being equal to 0.0152 grm. citral, the percentage proportion of citral in the oil is expressed by the following formula

$$\frac{(a - b) \cdot 1.52}{s}$$

The object of the extraction with benzene is to reclarify the solution, which becomes turbid after the addition of the hydrochloric acid. When this has been done it is easier to recognise the change in the colour during the titration.

### Refractive Indices of Essential Oils.

The following table has been brought up to date, the figures having been determined at 20° except where otherwise stated.

<i>Acorus calamus</i> (sweet flag).....	1.5028 to 1.5150
Almond (bitter).....	1.5320 to 1.5446
Almond (bitter) (S.A.P.) .....	1.5420 to 1.5460
Angelica.....	1.4800 to 1.4820
Angostura bark.....	1.5060 to 1.5085
Aniseed.....	1.5535 to 1.5565
Bay leaf (Pimenta).....	1.4850 to 1.5860 (according to sp. gr.)
Bay leaf (Laurus).....	1.4785 to 1.4800
Bergamot.....	1.4640 to 1.4690
Buchu.....	1.4740 to 1.4870
Cajuput.....	1.4600 to 1.4660
Callitris (leaves).....	1.4745 to 1.4815
Caraway.....	1.4870 to 1.4975
Cardamom.....	1.4610 to 1.4700
Cassia.....	1.5880 to 1.6045
Cassie (flowers).....	1.5120 to 1.5140
Cedar wood.....	1.4980 to 1.5050
Cedar wood (Libanon).....	1.5125 to 1.5134
Chamomile (Anthemis).....	1.4450 to 1.4525
Cinnamon bark.....	1.5900 to 1.5995
Cinnamon leaf.....	1.5350 to 1.5400
Citronella (Ceylon).....	1.4650 to 1.4680
Citronella (Java and Singapore).....	1.4800 to 1.4835
Citron.....	1.4745 to 1.4755
Clove (buds).....	1.5300 to 1.5360
Cognac.....	1.4290 to 1.4300

Copaiba (Angostura).....	I. 5010 to I. 5030
Copaiba (Bahia).....	I. 4940 to I. 4975
Copaiba (Cartagena).....	I. 4950 to I. 5010
Copaiba (Maracaibo).....	I. 4975 to I. 5000
Copaiba (Maturin).....	I. 4975 to I. 5015
Copaiba (Para).....	I. 4930 to I. 5025
Coriander.....	I. 4660 to I. 4675
Cubeb.....	I. 4909 to I. 4965
Cumin.....	I. 5040 to I. 5060
Cypress (leaves).....	I. 4700 to I. 4815
Dill.....	I. 4800 to I. 4950
Eucalyptus (B.P. and U.S.P. types).....	I. 4600 to I. 4675
Fennel.....	I. 5250 to I. 5345
Galangal.....	I. 4795 to I. 4815
Geranium (Pelargonium).....	I. 4620 to I. 4720
Geranium (Cymbopogon).....	I. 4720 to I. 4768
Ginger.....	I. 4880 to I. 4950
Gingergrass.....	I. 4780 to I. 4930
Guaiac wood (Bulnesia) at 30°.....	I. 5030 to I. 5050
Gurjun balsam.....	I. 4940 to I. 5025
Hop.....	I. 4850 to I. 4920
Juniper (berry).....	I. 4769 to I. 4835
Kananga.....	I. 4810 to I. 5110
Laurel ( <i>Laurus nobilis</i> : leaves).....	I. 4650 to I. 4770
Lavender.....	I. 4620 to I. 4670
Lemon.....	I. 4745 to I. 4760
Lemongrass.....	I. 4820 to I. 4885
Lime oil (distilled).....	I. 4750 to I. 4780
Lime oil expressed.....	I. 4800 to I. 4845
Linaloe.....	I. 4610 to I. 4630
Mace.....	I. 4760 to I. 4800
Marjoram.....	I. 4750 to I. 4850
Marjoram (Cretic).....	I. 5050 to I. 5105
Matico.....	I. 4960 to I. 5290
Melissa.....	I. 4738 to I. 4820
<i>Michelia longifolia</i> (flowers).....	I. 4500
Mustard.....	I. 5250 to I. 5281
Neroli.....	I. 4748 to I. 4765
Nutmeg.....	I. 4760 to I. 4800
Orange.....	I. 4725 to I. 4760
Orange (Tangerine).....	I. 4760 to I. 4790
Orris (liquid).....	I. 4940 to I. 4960
Paraley.....	I. 4800 to I. 5190
Patchouli.....	I. 5110 to I. 5150
Pennyroyal.....	I. 4800 to I. 4825
Pepper.....	I. 4890 to I. 4990
Peppermint.....	I. 4640 to I. 4679
Peru balsam.....	I. 5730 to I. 5790
<i>Persea gratissima</i> (leaves).....	I. 5139 to I. 5175
Pimento.....	I. 5303 to I. 5309
Pine needles.....	I. 4725 to I. 4835
Rose (at 25°).....	I. 4580 to I. 4650
Rosemary.....	I. 4670 to I. 4735
Rue.....	I. 4300 to I. 4340
Santalwood.....	I. 5050 to I. 5100
Sassafras.....	I. 5200 to I. 5300
Savin.....	I. 4730 to I. 4790
Saw palmetto.....	I. 4120 to I. 4135
Snake root.....	I. 4850 to I. 4900
pearmint.....	I. 4800 to I. 4970
pike lavender.....	I. 4650 to I. 4675
Storax (Asia Minor).....	I. 5395 to I. 4655
Sweet birch.....	I. 5350 to I. 5380
Thuja (leaf).....	I. 4574 to I. 4585
Thyme.....	I. 4800 to I. 4900
Tolu balsam.....	I. 5440 to I. 4600
Turpentine.....	I. 4690 to I. 4740
Vetivert.....	I. 5150 to I. 5270
Wintergreen.....	I. 5350 to I. 5375

Witch-hazel.....	1.4830 to 1.4895
Wormseed (American).....	1.4740 to 1.4760
Wormwood.....	1.4600 to 1.4710
Ylang-Ylang.....	1.4780 to 1.5125
Zedoary.....	1.5020 to 1.5060

### Alcohols of the Geraniol Series.

**Geraniol.**—In reference to the constitution of geraniol as given on page 258 of Vol. IV, it is still unsettled whether that formula is correct or whether geraniol should be represented as follows:



A corresponding alternative formula for the stereoisomer nerol (page 263, Vol. IV) naturally follows.

**Citronellol.**—An alternative formula for citronellol (see page 263, Vol. IV) has been suggested as follows:



The chemistry of citronellol is in a somewhat unsettled condition. Rupe<sup>1</sup> has clearly shown that citronellal exists in two modifications, and this may well be true of citronellol. Tiemann and Schmidt<sup>2</sup> held that *laevo*-citronellol from geranium and rose oils and *dextro*-citronellol obtained from citronellal are merely optically active isomers, whilst Barbier and Bouveault,<sup>3</sup> Bouveault and Gourmand,<sup>4</sup> and Barbier and Léser<sup>5</sup> maintain that they are two alcohols of different constitution. Barbier and Locquin<sup>6</sup> have now carried out a further series of experiments with a view to show that citronellol and rhodinol are in fact chemical isomers. They state that by attaching a halogen acid to *d*-citronellol or *l*-citronellol, treating the resulting compound with glacial acetic acid and sodium acetate, and subsequently hydrolysing, *d*-rhodinol or *l*-rhodinol results. They also claim that rhodinol on oxidation yields an aldehyde, rhodinal, which is not identical with citronellal.

**Linalol.**—The figures usually recorded for the sp. gr. of linalol are now known to be too high. Schimmel & Co. have prepared a pure specimen by decomposing linalol phenylurethane. Its sp. gr. at 15° was found to be 0.8666.<sup>7</sup> Tiemann<sup>8</sup> also found this to be the case, his pure specimen having a sp. gr. 0.8622 at 20°.

**Nerol.**—The view that geraniol (*q.v.*) and nerol are stereoisomers ex-

<sup>1</sup> *Annalen*, 1914, 402, 149.

<sup>2</sup> *Ber.*, 1896, 29, 903.

<sup>3</sup> *Compt. rend.*, 1896, 122, 737, 793.

<sup>4</sup> *Compt. rend.*, 1904, 138, 1699.

<sup>5</sup> *Compt. rend.*, 1897, 124, 1308.

<sup>6</sup> *Compt. rend.*, 1913, 157, 1114.

<sup>7</sup> *Report*, Oct., 1911, 141.

<sup>8</sup> *Ber.*, 1898, 31, 834.

pressed on pages 262 and 263 in Vol. IV has been confirmed by Blumann and Zeitschel.<sup>1</sup>

**Nerolidol and Farnesol.**—These two substances are not, chemically, in any close relationship to the geraniol alcohols, but, as it is not necessary to deal in this work with the sesquiterpene alcohols as a class, and as these bodies are found in the same group of oils, they may be dealt with conveniently in this section.

**Nerolidol** is an alcohol of the formula  $C_{15}H_{26}O$  which is found in the high boiling fractions of neroli oil. Its odour is sweet, but not powerful, and it has recently been found to be the principal constituent of peruvial, an oil isolated from balsam of Peru by Thoms and believed by him to be a chemical individual.<sup>2</sup> Nerolidol boils at  $276-277^{\circ}$  or at  $128-129^{\circ}$  under 6 mm. and has a sp. gr. 0.880,  $[\alpha]_D + 13^{\circ}$ , and ref. index 1.48023.

**Farnesol** is a sesquiterpene alcohol, having the formula  $C_{15}H_{26}O$ , which has been isolated from a number of the natural flower ottos. It has been identified in the essential oils of cassie flowers (*Acacia farnesiana*), rose, ylang-ylang and ambrette seeds. Its odour reminds one strongly of that peculiar odour which runs through all pure Bulgarian otto of rose, and known to experts as the "honey" odour—an odour somewhat recalling that of honeysuckle flowers. There is also in it a suggestion of a heavy odour, characteristic of the sesquiterpene alcohols, of the Oriental type, somewhat resembling that of cedar wood.

Farnesol is an oil boiling at  $160^{\circ}$  under 10 mm. pressure, and  $149^{\circ}$  under 4 mm. Its sp. gr. is about 0.890, and ref. index 1.4880. It is optically inactive. These characters indicate that it is more closely allied to the so-called olefinic sesquiterpenes than to the normal sesquiterpenes, which have a sp. gr. considerably over 0.900, and a ref. index of 1.500 or more.

Farnesol may be characterised by converting it by oxidation with chromic acid as described under the oxidation of geraniol, when it yields an aldehyde, which has been termed *farnesal*. This compound yields a semi-carbazone in the usual manner, m. p.  $133^{\circ}-135^{\circ}$ .

### Cyclic Terpene Alcohols.

**Borneol.**—The highest rotatory power observed for a natural borneol is  $[\alpha]_D - 39^{\circ} 25'$  (*Schimmel's Report*, April, 1895, 74). To differentiate between borneol and isoborneol, Henderson and Heilbron<sup>3</sup> recommend preparing the nitrobenzoates of the alcohols. The alcohol, dissolved in from 10 to 15 times its weight of pyridine is heated on the water-bath with about the calculated quantity of *p*-nitrobenzoyl chloride. The pyridine is extracted with diluted sulphuric acid, at  $0^{\circ}$ , and the *p*-nitrobenzoate washed with

<sup>1</sup> *Ber.*, 1911, 44, 2591.

<sup>2</sup> *Schimmel's Report*, April, 1914, 80.

<sup>3</sup> *Proc. Chem. Soc.*, 1913, 381.

dilute sulphuric acid, dried, and recrystallised from alcohol. The borneol compound melts at  $137^{\circ}$  and the isoborneol compound at  $129^{\circ}$ .

**Fenchyl Alcohol.**—This alcohol forms a phthalic acid ester, m. p.  $145^{\circ}$ , and phenylurethane, m. p.  $82-83^{\circ}$ .

Pickard, Lewcock and Yates<sup>1</sup> have prepared pure *laevo*-fenchyl alcohol, by reducing fenchone and converting the fenchyl alcohol into the hydrogen phthalate. By fractional crystallisation of the magnesium and cinchonine salts, a hydrogen phthalate was obtained, which, on saponification gave *laevo*-fenchyl alcohol  $[\alpha]_D - 15^{\circ} 30'$ .

**Thujyl Alcohol.**—For the isomeric forms of thujyl alcohol reference should be made to a paper by Paolini.<sup>2</sup>

**Terpineol.**—The liquid terpineol of commerce manufactured from terpin hydrate by the action of dilute sulphuric acid consists of a mixture of  $\alpha$ -terpineol, m. p.  $35^{\circ}$ , which predominates, and of  $\beta$ -terpineol m. p.  $32^{\circ}$  (incorrectly described as *p*-terpineol on page 281 of Vol. IV, line 2), and of liquid terpineol<sup>3</sup> m. p.  $-1^{\circ}$ . The terpineol melting at  $69-70^{\circ}$  has been termed  $\gamma$ -terpineol. The three varieties have the following characters:

	$\alpha$	$\beta$	$\gamma$
M. p. ....	$35^{\circ}-38^{\circ}$	$32^{\circ}-33^{\circ}$	$69^{\circ}-70^{\circ}$
Sp. gr. ....	0.935-0.940	0.923	.....
Rotation.....	up to $-117^{\circ}$	.....	.....
Ref. index.....	1.4810-1.4827	1.4747	.....
B. p.....	$217-219^{\circ}$	$210^{\circ}$	.....

**Menthol.**—Absolutely pure menthol melts, according to Schimmel & Co. (*Die Ätherischen Öle*, Band I, p. 405) at  $43.5^{\circ}$  to  $44.5^{\circ}$ . The specific rotatory power of melted menthol at  $46^{\circ}$  is  $-50^{\circ}$ , and in a 20% alcoholic solution at  $20^{\circ}$ , is  $-49.35^{\circ}$ . For the characters of isomenthol see Pickard and Littlebury.<sup>4</sup>

**Cineol.**—This neutral substance is incorrectly classed as an alcohol on page 284 of Vol. IV.

Alcohol	Source	M. p.	B. p.	Rotation $[\alpha]_D$	Ref. index	Sp. gr.
Amyrol.....	W. Indian santal oil	liquid	$300^{\circ}$	.....	.....	.....
Atractylol.....	Atractylis oil	$59^{\circ}$	$292^{\circ}$	0°	1.5110	.....
Betulol.....	Betula oil	liquid	$293^{\circ}$	$-35^{\circ}$	1.5018	0.975
Cedrol.....	Cedarwood oil	$86-87^{\circ}$	$294^{\circ}$	$+9.5^{\circ}$	1.5139	1.0056 (at $20^{\circ}$ )
Cubeb-camphor....	Cubeb oil	$68-70^{\circ}$	$248^{\circ}$	.....	.....	.....
Eudesmol.....	Eucalyptus oil	$88^{\circ}$	$284^{\circ}$	$-35.5^{\circ}$	1.5164	0.9884
Farnesol.....	Flower oils	liquid	$160^{\circ}$ (10 mm.)	0°	1.4881	0.887
Guaiol.....	Bulnesia oil.	$91^{\circ}$	$288^{\circ}$	$-30^{\circ}$	1.5100	0.971
Ledum-camphor....	Marsh tea oil	$104^{\circ}$	$281^{\circ}$	.....	1.5072	0.9814
Nerolidol.....	Neroli oil	liquid	$277^{\circ}$	$+13.5^{\circ}$	.....	.....
Patchouli-camphor..	Patchouli oil	$56^{\circ}$	$296^{\circ}$	$-97.6^{\circ}$	1.5245	1.028
$\alpha$ -Santalol.....	Santal oil	liquid	$301^{\circ}$	$-1.2^{\circ}$	.....	0.977
$\beta$ -Santalol.....	Santal oil	liquid	$310^{\circ}$	$-56^{\circ}$	.....	0.9784

<sup>1</sup> *Proc. Chem. Soc.*, 1913, 29, 127.

<sup>2</sup> *Rend. R. Acad. Lincei*, 20, 1, 765.

<sup>3</sup> Wallach, *Liebig's Annalen*, 1907, 356, 218; 1908, 362, 342.

<sup>4</sup> *Trans.*, 1912, 1019, 10.

### Sesquiterpene Alcohols.

The preceding table brings the principal characters of the sesquiterpene alcohols up to date.

### Aldehydes of the Geraniol Series.

**Citral.**—It is uncertain whether citral has the constitution assigned to it on page 267 of Vol. IV, or whether it is represented by the following formula:



**Citronellal.**—Rupe<sup>1</sup> has shown that there exist two isomeric forms of citronellal.

### ERRATA IN VOL. IV.

Pages 180 and 315, Pinene does not form a constituent of oil of bay and its presence in such oil is a sign of adulteration.

Page 182, line 12, for "derivations" read "derivatives."

Page 189, line 12 from bottom, for "Thorns" read "Thoms."

Page 210, line 1 of footnote, for "Thomas" read "Thoms."

Page 233, line 17, for "Cassio" read "Cassia" and add "See Vol. III, p. 442."

Page 224, in Table, for "Anethol" read "Anethole."

Page 281, line 2, for "*p*-terpineol" read "*β*-terpineol."

<sup>1</sup> *Annalen*, 1914, 402, 149.

SPECIAL CHARACTERS OF ESSENTIAL OILS.

By ERNEST J. PARRY, B.Sc., F.I.C.

ANDROPOGON OILS.

Most of these oils are now referred to the genus *Cymbopogon* which was formerly recognized only as a subgenus.

**Citronella Oil.**—The parent plant of citronella grass is known as mana grass of which Stapf distinguishes two varieties, *Cymbopogon Nardus*, var. *Linnæi*, and *C. Nardus* var. *confertiflorus*. The natives differentiate still further in Ceylon and the following table illustrates this differentiation, with the character of the various oils themselves.

No.	Parent Plant		d <sub>15</sub>	α <sub>D</sub>	Total alcohol %	Geraniol %	Citronellal %
	Botanical name (According to Stapf's determination)	Native name					
1	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Maha-naran-pengiri	0.920	— 3° 7'	51.6	27.6	24.0
2	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Maha-naran-pengiri	0.905	— 6° 32'	63.2	38.4	24.8
3	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Maha-naran-pengiri	0.912	+ 3° 22'	57.2	36.2	21.0
4	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Heen-naran-pengiri	0.913	+ 2° 35'	43.5	24.6	18.9
5	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Heen-naran-pengiri	0.894	— 3° 20'	47.7	25.8	21.9
6	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Heen-naran-pengiri	0.909	+ 2° 6'	53.5	30.0	23.5
7	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Light-leaved mana	0.909	+ 4° 54'	56.5	38.6	17.9
8	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Light-leaved mana	0.908	+ 3° 30'	64.0	30.2	33.8
9	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Small-leaved mana	0.906	+ 3° 7'	57.0	34.4	22.6
10	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Small-leaved mana	0.909	+ 3° 20'	56.3	36.5	19.8
11	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Sour mana	0.935	+ 16°	35.3	16.3	19.0
12	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Sour mana	0.967	+ 15° 50'	26.9	6.3	20.6
13	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Very broad-leaved mana	0.926	+ 1° 31'	48.7	25.8	22.9
14	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Very broad-leaved mana	0.906	— 0° 24'	64.7	36.5	28.2
15	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Given as "maha-pengiri," but probably "mana"	0.912	— 1° 38'	48.6	25.5	23.1
16	<i>C. Nardus</i> , Rendle var. <i>Linnæi</i> , Stapf ( <i>typicus</i> )	Given as "maha-pengiri," but probably "mana"	0.909	— 2° 18'	56.4	35.8	20.6
17	<i>C. Nardus</i> , Rendle var. <i>confertiflorus</i> , Stapf	Glaucous-leaved- mana	0.913	+ 12° 12'	46.5	29.3	17.2



No.	Parent Plant		d <sub>15</sub>	α <sub>D</sub>	Total alcohol %	Geraniol %	Citronellal %
	Botanical name (According to Stapf's determination)	Native name					
18	<i>C. Nardus</i> , Rendle var. <i>confertiflorus</i> , Stapf	Glaucous-leaved-mana	0.900	+ 4°	61.2	43.7	17.5
19	<i>C. Nardus</i> , Rendle var. <i>confertiflorus</i> , Stapf	White-stemmed mana	0.908	+ 1° 27'	54.8	30.2	24.6
20	<i>C. Nardus</i> , Rendle var. <i>confertiflorus</i> , Stapf	White-stemmed mana	0.904	+ 2° 26'	58.0	24.8	33.2
21	<i>C. Nardus</i> , Rendle var. <i>confertiflorus</i> , Stapf	Red-stemmed mana	0.929	+ 6° 19'	39.1	19.4	19.7
22	<i>C. Nardus</i> , Rendle var. <i>confertiflorus</i> , Stapf	Red-stemmed mana	0.909	+ 0° 58'	57.0	28.9	28.1
23	<i>C. Nardus</i> , Rendle, closely allied to var. <i>confertiflorus</i>	Lenabatu-pengiri (not genuine)	0.915	+ 2° 46'	52.0	31.1	20.9
24	<i>C. Nardus</i> , Rendle, closely allied to var. <i>confertiflorus</i>	Lenabatu-pengiri (not genuine)	0.902	- 2° 11'	63.1	39.5	23.6
25	<i>C. Nardus</i> , Rendle, closely allied to var. <i>confertiflorus</i>	Lenabatu-pengiri (not genuine)	0.907	- 0° 6'	64.2	44.8	19.4

The Maha-pengiri grass, which is cultivated largely in Java is *Cymbopogon Winterianus*.

The constituents of Ceylon citronella oil hitherto identified are as follows: citronellal, geraniol, camphene, dipentene, methyl-heptenone, borneol, methyl-eugenol, limonene, thujyl alcohol (?), nerol, geranyl acetate, *d*-citronellyl acetate and butyrate and a sesquiterpene of sp. gr. 0.8643, probably identical with an aliphatic sesquiterpene isolated by Semmler and Spornitz<sup>1</sup> from Java citronella oil, and which has the following characters: sp. gr. 0.8489, optical rotation +0° 36', ref. index 1.5325, and b. p. 138-140° at 9 mm. pressure. Elze<sup>2</sup> has quite recently isolated about 0.25% of farnesol from this oil. The Java oil contains geraniol, citronellal, *d*-citronellol, traces of methyl-eugenol, citral, isovaleric aldehyde, *iso*-amyl-alcohol and the sesquiterpene, citronellene, above mentioned. The following figures may be taken to cover the vast majority of genuine samples. But it must be remembered that practically the whole of the oil exported in drums from Ceylon is adulterated with petroleum—so as just to pass Schimmel's test. The custom of purchasing on a geraniol standard (*i.e.*, total acetylisable constituents) is rapidly gaining ground.

	Ceylon oil	Java oil
Sp. Gr.....	0.898 to 0.920	0.884 to 0.900
Optical rotation.....	- 7° to - 20°	0° to - 3°
Ref. index at 20°.....	1.4790 to 1.4890	1.4650 to 1.4720
Total "Geraniol".....	57 % to 64 %	83 % to 96 %

**Lemon-grass Oil.**—Formerly it was true that lemon-grass oil distilled in the East was soluble in 3 volumes of 70% alcohol, whereas that distilled in the West Indies, although soluble when freshly distilled rapidly lost its solubility. This is not, however, true today, and nearly all lemon-grass oil

<sup>1</sup> Ber., 1913, 46, 4025.  
<sup>2</sup> Chem. Zeit., 1913, 37, 1422.

is at the present time insoluble in 3 volumes of 70% alcohol. Further, on the voyage from the East it steadily loses its citral strength and samples examined a year after distillation will frequently show a loss of 5 to 8% in citral. Whether this is due to the use of different types of grass, or different method of cultivation is not yet understood.

Numerous samples of lemon-grass oil from various parts of the world have recently been examined, such as Uganda, Bermuda, Montserrat, Seychelles, Sumatra, Mayotte and Burmah. These, however, are scarcely commercial articles and call for no remarks here.

**Palmarosa Oil and Ginger-grass Oil.**—The grass known as *Cymbopogon Martini* exists in two varieties, the native names being “motia” and “sofia.” These names have been adopted by Burkill, and the grasses are known as follows:

*Cymbopogon Martini* var. *Motia* = palmarosa oil  
*Cymbopogon Martini* var. *Sofia* = ginger-grass oil.

The characters of the two oils are as follows:

	Palmarosa	Ginger-grass
Sp. Gr.....	0.886 to 0.900	0.900 to 0.953
Optical rotation.....	+6° to -3°	+54° to -30°
Ref. index.....	1.4720 to 1.4760	1.4780 to 1.4930
Acid value.....	0.5 to 3.0	to 6.2
Ester value.....	12 to 48	8 to 29 (rarely to 54)
Total geraniol.....	75 to 95 %	35 to 65 %
Solubility in 70 % alcohol.....	1 in 1.5 to 3 volumes	1 in 2 to 3 volumes

Traces of farnesol have been found in palmarosa oil,<sup>1</sup> and also traces of caproic acid in the form of esters.

Ginger-grass oil contains *d*- $\alpha$ -phellandrene, dipentene, *d*-limonene, heptaldehyde, citronellal or an isomeric aldehyde, *i*-carvone, geraniol and dihydrocuminic alcohol.

**Vetivert Oil.**—This oil is distilled from the roots of *Vetiveria zizanioides*, formerly known as *Andropogon muricata*. It is a viscous oil with a heavy, penetrating odour, and is used to a considerable extent in the manufacture of perfumes of the oriental type. The roots are known in India by the name of Khas-Khas or cus-cus.

Genvresse and Langlois isolated from this oil a hydrocarbon  $C_{15}H_{24}$  which they termed *vetivene* and an alcohol, *vetivenol*,  $C_{15}H_{26}O$  and an ester of this alcohol and an acid of the formula  $C_{15}H_{24}O_2$ . Semmler and his colleagues<sup>2</sup> have more recently shown that vetivenol has the formula  $C_{15}H_{24}O$ , and the acid  $C_{15}H_{22}O_2$ . For the differences between the alcohol and esters present in vetivert oils of different origins, the original paper should be consulted.

<sup>1</sup> Else, *Chem. Zeit.*, 1910, 34, 857.

<sup>2</sup> *Compt. rend.*, 1902, 135, 1059.

<sup>3</sup> *Ber.*, 1912, 45, 2347.

The oil distilled in Europe from the dried imported root has the following characters:

Sp. gr.....	1.015 to 1.040
Optical rotation.....	+25° to +37°
Ref. index to 20°.....	1.5220 to 1.5270
Acid value.....	27 to 65
Ester value.....	9.8 to 23
Ester value after acetylation.....	130 to 158

It is soluble in 1 to 2 volumes of 80% alcohol with turbidity.

The oil distilled in Réunion from the fresh roots has the following characters:

Sp. gr.....	0.980 to 1.020
Optical rotation.....	+22° to +37°
Ref. index.....	1.5150 to 1.5270
Acid value.....	4.5 to 17
Ester value.....	5 to 20
Ester value after acetylation.....	124 to 145

It is soluble in 1 to 2 volumes of 80% alcohol with turbidity.

Fiji and Seychelles vetivert oils do not differ materially from the above described.

Puran Singh<sup>1</sup> has examined the oil distilled in India from Indian-grown roots, and his results suggest that in the distillation of the roots a small amount of resin is carried over, and that if the oil be freed from this by careful redistillation, the resulting oil is lævorotatory. 75 gm. of oil were carefully steam distilled and about 65 gm. of oil resulted. The residue was a dark-red resinous mass, which was extracted with alcohol. About 9.4 gm. of a dark-red resin of a brilliant fracture were obtained. It softened at 65°, and completely melted at 70°. It gave the following constants:

Sp. gr. at 30°.....	1.132
Acid number.....	46.92
Saponification number.....	111.02
Ester number.....	64.28
Iodine value (Häbl, after 18 hours).....	268.20
Optical rotation-calculated on 10 c.c. of the solid resin.....	+488.04

The redistilled oil, which was of a yellowish-brown colour and quite transparent, gave the following constants:

Sp. gr. at 15°.....	1.011
Optical rotation in 100-mm. tube.....	-30.65
N <sub>D</sub> 20°.....	1.5165
Acid number.....	10.5
Saponification number.....	80.1
Ester number.....	69.6
Saponification number after acetylation.....	132.8
Iodine value (Häbl, after 18 hours).....	194.4
Soluble in 2 parts of 80% alcohol.	

The above constants are different from those already recorded by various observers. This difference may be due to the elimination of the resin from the oil by redistillation; at least in optical rotation it is mainly due to this cause. The angle of rotation of the oil in this case is about -31°, while all observers have recorded for vetivert oil a rotation of +25° to +40°. The optical rotation of the resin is +488.4°. Taking the proportion of the oil to

<sup>1</sup> *Chem. and Druggist*, 1914, 2, 51.

<sup>2</sup> Approximately; because the solution had to be made too dilute for observation, owing to the very dark colour of the resin.

resin, as it is in this case, to be 8:1, the optical rotation calculated on the mixture of resin and oil comes to  $+34^{\circ}$ . It seems that the dextrorotation of the oil is due to the small proportion of *Khas-Khas* resin. This will also have its effect on other constants. It is not known whether the constants of this oil as recorded by other observers were determined on redistilled oil or on the first distillate. If on the latter, then the constants of this resin-free oil will in all cases be different from those already published. This has yet to be confirmed.

### Almond Oil.

Essential oil of bitter almonds is a commercial product of considerable importance, as it is used to a large extent in the preparation of flavouring essences.

The true bitter almond oil is obtained by distillation from the seeds of *Prunus amygdalis* (*Amygdalis communis*), the ordinary bitter almond. But as the kernels of the peach and apricot yield an oil which is indistinguishable from that of the almond, it is certain that much of the almond oil of commerce is really derived from peach and apricot kernels. Hence the remarks made here apply to all three oils indiscriminately.

The oil does not exist as such in the seeds but is produced by the action of the enzyme emulsin on the glucoside amygdalin, under the influence of water. Without discussing the question of intermediate products, the action taking place results, in the main, in the formation of benzaldehyde and hydrocyanic acid as follows:



The natural oil therefore contains hydrocyanic acid and is highly poisonous. The commercial article is therefore usually deprived of hydrocyanic acid and sold as "Ol. amygdalæ essent. sine acido prussico (S.A.P.)."

**Composition.**—This oil consists principally of benzaldehyde (with or without hydrocyanic acid) and a little benzaldehyde-cyanhydrin,  $\text{C}_6\text{H}_5(\text{CH})(\text{OH})\text{CN}$  formed by the interaction of the aldehyde and the acid.

**Characters.**—The sp. gr. of the natural oil varies between 1.045 and 1.070. It is optically inactive or at most, very faintly dextrorotatory, up to  $+0^{\circ} 10'$ . Its ref. index is from 1.5320 to 1.5440.

Hydrocyanic acid is detected by shaking the oil with water, and then adding to the water minute quantities of ferrous and ferric chlorides, and then solution of caustic potash. On adding hydrochloric acid a blue colour or precipitate is formed if hydrocyanic acid be present. To estimate the hydrocyanic acid, 1 gram. should be dissolved in 5 c.c. of alcohol and 50 c.c. of water added. An ammoniacal solution of silver nitrate is then added, and the whole well shaken. The liquid is then acidified with nitric acid, and the silver

cyanide is collected, washed and weighed as silver after ignition. Four parts of silver correspond to one of hydrocyanic acid.

If deprived of hydrocyanic acid, the oil has a sp. gr. 1.050 to 1.055, and a ref. index of 1.5420 to 1.5460 at 20°. It boils principally at 179° and is soluble in 1 to 2 volumes of 70% alcohol. Nitrobenzene has been found as an adulterant of this oil, but is rarely used now. Its sp. gr. is about 1.200 and its odour is characteristically coarse. It can be detected with certainty by boiling the oil with a little acetic acid and iron filings. The nitrobenzene is reduced to aniline, which is distilled off and a few drops of chlorinated lime solution added to the distillate; the characteristic violet colour results if aniline be present. The usual adulterant, however, is synthetic benzaldehyde. This can be detected, chemically, only if it contains traces of chlorine, which the lower grades do, having been made by a condensation process in which hydrochloric acid is used. To detect chlorine, a pure filter paper is saturated with the oil and placed in a small porcelain dish, standing in a larger one, and a beaker whose sides are moistened with distilled water is inverted over the smaller dish after the paper has been lighted. The beaker is washed out with a few drops of distilled water, and the liquid filtered, and the filtrate tested for chlorides in the usual manner. Heyl<sup>1</sup> recommends the following method:

1 to 2 grm. of chlorine-free calcium hydroxide are stirred up with a glass rod in a small porcelain dish with 10 to 15 drops of benzaldehyde, the mixture is then covered with a thin layer of calcium hydroxide and slowly brought to a red heat. After cooling, the contents of the dish are poured into a beaker, 5 to 6 c.c. of water are carefully added, and the mixture is faintly acidified with nitric acid. The solution is then filtered through chlorine-free filtering paper or glass-wool and tested for chlorine with silver nitrate. Rupp<sup>2</sup> prefers the following test:

A copper wire, or, better still, a strip of copper wire-netting 0.5 cm. in width (about 1 mm. mesh) is twisted at one end into a narrow spiral shape, forming a roll about the diameter of a large pea. This roll is repeatedly drawn through a non-luminous flame in order to oxidise the surface of the copper and to remove any yellow or green colouration. When cool, the roll is dipped into the benzaldehyde under examination and is then exposed to the flame for a moment in order to inflame the benzaldehyde. When the benzaldehyde is burnt off (not in the flame) the roll is again applied to the top of the flame. If there is a green colouration, chlorine is present.

### Angelica Oil.

Schimmel & Co.<sup>3</sup> give the following values for angelica oil distilled by themselves from various parts of the plant.

<sup>1</sup> *Apoth. Zeit.*, 1912, 27, 49.

<sup>2</sup> *Apoth. Zeit.*, 1912, 27, 49.

<sup>3</sup> *Report*, April, 1911, 20.

Oil from	Sp. gr. at 15°	Rotation	Ref. index at 20°.	Acid No.	Ester No.
Leaves.....	0.8550	+28° 2'	1.4778	0.5	17.6
Leaves.....	0.8697	+22° 8'	1.4804	1.3	22.6
Leaves.....	0.8767	+20° 11'	1.4832	1.6	21.1
Root.....	0.8733	+28° 23'	1.4808	2.5	25.9
Seed.....	0.8623	+12° 12'	1.4868	1.1	18.1

### Aniseed Oil.

Schimmel & Co.<sup>1</sup> have identified the following terpenes in oil of star aniseed: *d*- $\alpha$ -pinene; *d*- $\beta$ -phellandrene; dipentene; *l*-limonene.

Contrary to the statement made on page 312 of Vol. IV, the solidifying point of aniseed oil is a factor of the highest importance. The fact that the oil can exist in the liquid condition at a temperature much below its congealing point is immaterial, since crystallisation can be induced by sowing the oil with a crystal of anethole, or by skilful stirring with the thermometer. If the oil, in a narrow test-tube, be cooled to about 9° or 10°, and a crystal of anethole added, or crystallisation induced by stirring, the thermometer will rapidly rise as crystallisation sets in, and the maximum temperature, which a little experience will readily determine, indicates the true congealing point. In the best oils this will be at least 15°, and congealing points below this indicate inferior oils, or oils from which anethole has been deliberately extracted.

The presence of petroleum oil in aniseed oil is very easily detected by the lowering of the sp. gr., the lowering of the melting point and ref. index, and the insolubility in even large quantities of 90% alcohol, when petroleum oil separates and can be examined and identified.

A number of samples have of recent years been found on the market which have either been adulterated with such an oil as camphor oil or from which large quantities of anethole have been abstracted; see Parry,<sup>2</sup> Umney<sup>3</sup>, Jensen<sup>4</sup> and Durrans.<sup>5</sup> It is still a question of doubt as to which form of adulteration had been adopted, but Parry recommends dividing the oil into the following fractions: the first = 10%, the three following = 25% each, and the residue = 15%. The following tables show the melting point and ref. index of a normal oil and one suspected by Parry of being adulterated by the addition of such an oil as heavy camphor oil, and the same figures for a normal oil and an oil from which anethole had purposely been abstracted, as illustrating Messrs. Schimmel & Co.'s views that the adulteration has been due to abstraction of anethole.

The figures in the following tables for normal oils will be found useful in judging aniseed oils which are at all doubtful, apart from whether the adulteration is by addition of a foreign oil or by the abstraction of anethole.

<sup>1</sup> Report, October, 1911, 86.

<sup>2</sup> Chemist and Druggist, 1910, 77, 687.

<sup>3</sup> Perf. and Ess. Oil Record, 1910, 1, 236.

<sup>4</sup> Pharm. J., 1910, 85, 759.

<sup>5</sup> Perf. and Ess. Oil Record, 1911, 2, 60.

PARRY.

Nr.	Amount of fraction	Normal star anise oil (m. p. 18°)		Suspected star anise oil (m. p. 12.5°)	
		M. p.	n <sub>D20</sub> to 21°	M. p.	n <sub>D20</sub> to 21°
1	10 %	8°	1.5316	-3°	1.5125
2	25 %	18°	1.5500	15°	1.5419
3	25 %	20°	1.5540	17.5°	1.5500
4	25 %	20°	1.5591	18°	1.5521
5 (Residue)	15 %	15°	1.5522	11°	1.5467

SCHIMMEL & CO.

Nr.	Amount of fraction	Normal star anise oil (sol. p. 16.5°)		The same oil after abstraction of part of its anethole (sol. p. 10.1°)	
		Sol. p.	n <sub>D20</sub> °	Sol. p.	n <sub>D20</sub> °
1	10 %	7.5°	1.53279	under 0°	1.50326
2	25 %	15.7°	1.55125	8.1°	1.53885
3	25 %	18.9°	1.55866	14.5°	1.55342
4	25 %	19.4°	1.55980	15.2°	1.55723
5 (Residue)	15 %	7.5°	1.56079	under 0°	1.55505

Bay Oil.—The oil from Californian Bay (Vol. IV, p. 316) has the following characters:

Sp. gr.....	0.930 to 0.950
Optical rotation.....	-22° to -24°
Acid value.....	about 5
Ester value.....	about 5
Ester value after acetylation.....	about 50

It is soluble in 1.5 to 2.5 volumes of 70% alcohol. This oil contains eugenol, *l*- $\alpha$ -pinene, safrole, methyl-eugenol, and about 40 to 60% of *umbellulone*, a ketone of sp. gr. 0.950 at 20°, optical rotation - 36° 30', ref. index 1.48325, and b. p. 219-220°. It forms a semi-carbazone melting at 240°-243°.¹

Bergamot Oil.—The principal adulteration of Bergamot oil today is by the addition of artificial esters together with a neutral body such as lemon terpenes. The detection of these is fully described under “*Esters*” (on pages 330-336). A pure bergamot oil should have the following characters:

Sp. gr.....	0.881 to 0.8865
Optical rotation.....	+8° to +24°
Ref. index at 20°.....	1.4650 to 1.4675
Fixed residue.....	4.3 to 6 %
Sap. value of residue.....	160 to 200
Acid value.....	1.0 to 3.8
Esters as linalyl acetate.....	34 to 43 %

The differences observed in the process of fractional saponification are given under “*Esters*” on page 331.

¹ Power and Lees, *Trans.*, 1904, 85, 629; also 1906, 89, 1104; 1907, 91, 271 and 1908, 93, 252.



### Buchu Oil.

The oil distilled from buchu leaves is employed to some extent in medicine. The species usually found in commerce are *Barosma betulina*, *B. crenulata*, and *B. serratifolia*.

Diosphenol,  $C_{10}H_{16}O_2$ , is the most characteristic constituent of the oil, occurring to a considerable extent in that from *B. betulina*, whilst only to a small extent in that of *B. serratifolia*. It is a crystalline solid, m. p.  $81^\circ$  and b. p.  $232^\circ$ . It is a cyclic keto-phenol and is also known as buchu-camphor. The tepenes, limonene and dipentene are present and also *l*-menthone. The oils of the three species above mentioned have the following characters:

	<i>B. betulina</i>	<i>B. crenulata</i>	<i>B. serratifolia</i>
Sp. gr. ....	0.937–0.970	0.9364	0.918–0.961
Rotation. ....	$-14^\circ$ to $-18^\circ$	$-15^\circ 22'$	$-12^\circ$ to $-36^\circ$
Ref. index. ....	1.4740 to 1.4870	1.4801	.....

The oils from *Barosma pulchella* and *B. venusta* have also been examined, but are not commercial articles.<sup>1</sup>

### Calamus Oil.

This oil is used, especially on the continent, as a flavouring material in the preparation of certain types of beers, liqueurs, etc. The European oil is distilled from the rhizome of *Acorus calamus*, whilst the Japanese oil is probably derived from *Acorus spurius*.

Russian calamus oil contains  $\alpha$ -pinene, camphor, a sesquiterpene, calamene (having a sp. gr. 0.922, optical rotation  $+5^\circ$  and ref. index 1.5057) and an alcohol  $C_{15}H_{24}O$ , which is termed *calamenenol*.<sup>2</sup> Traces of eugenol and heptylic acid are also present. Japanese calamus oil contains a small amount of methyl-eugenol. European calamus oil has a sp. gr. 0.958 to 0.970, optical rotation  $+9^\circ$  to  $+35^\circ$ ; ref. index 1.5028 to 1.5078, acid value 1 to 2.5; ester value 5 to 20, and ester value after acetylation 32 to 50. It is soluble in practically any quantity of 90% alcohol. Japanese calamus oil has a sp. gr. 0.985 to 1.000, optical rotation  $+7^\circ$  to  $+25^\circ$ , ester value about 4, ester value after acetylation, 17.

### Camphor Oil.

The following are the constituents of *normal* camphor oil, only a limited number of which are present in the fractions known commercially as camphor oil.

<sup>1</sup> Schimmel's Report, April, 1909, 96 and April, 1910, 17; Pharm. J., 1913, 90, 60.

<sup>2</sup> Semmeler and Spornitz, Ber., 1913, 46, 3700.

- (1) Acetaldehyde.

(2) *d*- $\alpha$ -pinene.

(3) Camphene.

(4) *d*-fenchene.

(5)  $\beta$ -pinene.

(6) Phellandrene.

(7) Cineol.

(8) Dipentene.

(9) *d*-limonene.

(10) Borneol.

(11) Camphor.

(12) Terpinenol.
- (13)  $\alpha$ -terpineol.

(14) Citronellol.

(15) Safr ole.

(16)  $\Delta'$ -menthenone-3.

(17) Carvacrol.

(18) Cumic alcohol.

(19) Eugenol.

(20) Bisabolene (sesquiterpene).

(21) Cadinene.

(22) Caprylic acid.

(23) An acid  $C_9H_{16}O_2$ .

(24) A blue oil.

In addition to the above bodies, which are given in the order of their boiling points, Semmler and Rosenberg<sup>1</sup> have isolated a sesquiterpene which they term sesquicamphene (sp. gr. 0.9015 at 20°, optical rotation + 3°, and refractive index 1.5006), and a sesquiterpene alcohol, which they name *sesquicamphenol*. A diterpene,  $C_{20}H_{32}$ , which has been named  *$\alpha$ -camphorene*, of sp. gr. 0.8870 at 20° and b. p. 178° under 6 mm., was also isolated.

Crude camphor oil has a sp. gr. 0.950 to 0.995, and is usually fractionated after removal of most of the camphor, in Japan, into white camphor oil and “red” or “black” camphor oil. White camphor oil has a sp. gr. 0.870 to 0.910, and black camphor oil from 0.990 to 1.036.

Cardamon Oil.

Cardamom oil is obtained from the seeds of several varieties of cardamoms. Of these the principal are those known as Ceylon-Malabars and Ceylon-Mysore, both being varieties of *Elettaria cardamomum*. The fruit known as “Ceylon wilds” is probably derived also from a variety of the same plant. Siam cardamom is the fruit of *Amomum Cardamomum*. Terpinyl acetate is an important constituent of the oil, as well as free terpineol and cineol. The following are the characters of the various oils:

	<i>Elettaria cardamomum</i>	Celon wilds	<i>Amomum cardamomum</i>
Sp. gr.....	0.923-0.944	0.895-0.906	0.905 at 42°
Rotation.....	+24° to +47°	+12° to +15°	+38°
Ref. index.....	1.4620-1.4670	.....	.....
Acid value.....	to 4	.....	0.8
Ester value.....	94-150	25-70	14-18.8
Solubility in 70 % alcohol.....	1 in 2 to 5 vols.	.....	.....

This oil is used to a certain extent in flavouring cakes, sauces and other food products.

Cassia and Cinnamon Oils.

Cassia oil is an oil largely employed in the perfuming of cheap soaps, etc. It is distilled from the leaves, twigs and other parts of *Cinnamomum cassia*, a native of Cochin China. The cinnamon oil of commerce is obtained from the bark of *Cinnamomum zeylanicum*, a native of Ceylon. The leaves of this tree also yield an essential oil, which is a commercial article.

<sup>1</sup> Ber., 1913, 46, 768.

**Cassia Oil.**—The principal constituent of this oil is cinnamic aldehyde, small quantities of a terpene, cinnamic esters and *o*-methyl-coumaric aldehyde being also present. It is customary to grade cassia oils on the market as 70–75, 75–80, and 80–85%, these values indicating the cinnamic aldehyde content. But as pure oils may, and probably usually do, contain from 85 to 90% or even more, it has become a recognised custom to standardise the lower grade oils with resin, so that a 70–75% oil will usually contain 71%, and 80–85% oil 81% of cinnamic aldehyde.

A pure cassia oil has a sp. gr. 1.055 to 1.070, optical rotation  $-1^{\circ}$  to  $+6^{\circ}$ , ref. index, 1.6020 to 1.6075, and acid value 6 to 15. It is easily soluble in 2 volumes of 80% alcohol.

The cinnamic aldehyde should be determined in a Hirschsohn flask, using 5 c.c. of oil and a hot 30–35% solution of sodium hydrogen sulphite. The flask is kept in a boiling water-bath until the whole of the crystals formed are dissolved, the flask being well shaken at frequent intervals. The unabsorbed oil is then forced into the neck of the flask by adding more of the solution and when cold, the oil is read off, the difference being calculated as cinnamic aldehyde. It is probable that this process gives slightly too high results, whilst the use of neutral sodium sulphite gives results about 3 to 4% lower. It has become an established trade custom, however, to return all results for this oil by the bisulphite process.

The influence of added resin is to raise the acid value of the oil considerably and to cause the oil to leave a high distillation residue. Cassia oils free from resin do not give appreciable precipitates with a saturated solution of lead acetate in alcohol.

The following is the best method of using the lead acetate test, and from the figures quoted<sup>1</sup> it will be seen that the higher the lead precipitate, the higher the acid value, and consequent percentage of added resin.

5 grm. of the oil are dissolved in 20 c.c. of 70% alcohol and 10 c.c. (or more if necessary) of a saturated solution of lead acetate are added. The precipitate is collected on a tared Gooch filter (packed with ignited asbestos) and thoroughly washed with 70% alcohol. The filtrate should be tested with more of the lead acetate solution and any further precipitate filtered off. The precipitate is dried at  $100^{\circ}$  to constant weight. Results obtained on prepared oils were as follows:

1. Cassia oil, containing 10% resin gave 10.6% lead ppt.
2. Cassia oil, containing 15% resin gave 15.2% lead ppt.
3. Cassia oil, containing 20% resin gave 19.7% lead ppt.

The determination of the acid value of cassia oil, suggested by Yates,<sup>2</sup> cannot be relied upon to indicate exactly the proportion of added resin, on account of the natural variation in the acid values of the oil and resin respectively, and one should hesitate to place reliance on this factor as a means

<sup>1</sup> *Perf. and Ess. Oil Record*, 1914, 7, 264.

<sup>2</sup> *Perf. and Ess. Oil Record*, 1912, page 83.

of judging the percentage of added resin, although it is significant that oils with a high aldehyde content have low acid values.

The following are typical examples of the results obtained:

	Aldehyde content	Acid value	Lead ppt.
1. Cassia oil free from resin.....	92	6	nil.
2. Cassia oil free from resin.....	88	13	nil.
3. Cassia oil containing resin.....	82	27	10.1
4. Cassia oil containing resin.....	73	29	10.1
5. Cassia oil containing resin.....	72	23	10.6

An approximate determination of added resin may be obtained by distilling 50 grm. in a small tared Wartz flask and stopping the distillation when the temperature reaches 280°. The residue should not exceed 10%, rarely over 8%, so that any excess may be regarded as resin.

**Cinnamon Bark Oil.**—Although the greater part of the world's supply of this oil comes from Ceylon, a certain amount is distilled, on a small scale in other countries, and Seychelles cinnamon oil has recently been carefully examined. Cinnamic aldehyde is the constituent present in largest quantity, but as this oil contains less aldehyde than cassia oil, whilst its 'odour is far sweeter and more delicate, it is obvious that much of the perfume value lies in the non-aldehydic portion of the oil. The oil contains, in addition, eugenol, methyl-amyl ketone, benzaldehyde, pinene, phellandrene, cymene, nonylaldehyde, cumic aldehyde, hydrocinnamic aldehyde, linalol, linalyl esters, and caryophyllene.

For slight differences in the composition of Seychelles cinnamon oil see Schimmel's Report, April, 1913, page 42. According to most authorities pure cinnamon oil has a sp. gr. 1.020 to 1.040, but Hill<sup>1</sup> and Umney and Bennett<sup>2</sup> consider that a lower sp. gr., from 0.994 to 1.022 is normal for pure cinnamon oil. Schimmel & Co. consider that these low sp. gr. are due to abnormal distillation, a certain amount of the aldehyde being oxidised and lost in the distillation. The oil is faintly lævorotatory, up to  $-1^{\circ}$ , and has a ref. index 1.5810 to 1.5910. It contains from 55 to 65% of cinnamic aldehyde (or according to Hill, Umney and Bennett, *loc. cit.*, between 50 and 60%); it should not contain more than 5–10% (rarely more than 6%) of eugenol, as determined by absorption with 5% potassium hydroxide solution. It is soluble in 2 to 3 volumes of 70% alcohol. The principal adulterants are clove leaf oil and synthetic cinnamic aldehyde.

**Cinnamon leaf oil** is distilled from the leaves of *Cinnamomum zeylanicum*. It closely resembles clove oil, containing from 70 to 90% of eugenol. Small quantities of cinnamic aldehyde and terpenes are present.

The pure oil has a sp. gr. 1.044 to 1.065, optical rotation  $-0^{\circ} 15'$  to  $+2^{\circ} 20'$ ; ref. index 1.5310 to 1.5400, and eugenol value from 70 to 90%.

**Celery Oil.**—All parts of the herb *Apium graveolens*, the common celery, yield an essential oil, of which that from the seeds is most valued. Schimmel

<sup>1</sup> *Chem. and Druggist*, 1910, 76, 959.

<sup>2</sup> *Perf. and Ess. Oil Record*, 1910, 1, 169.

& Co., state that from the green leaves most exactly reproduces the natural celery flavour. The oil from the seed is obtained to the extent of about 3%, as a liquid of strong celery odour, having a sp. gr. 0.870 to 0.895 and an optical rotation  $+65^{\circ}$  to  $+80^{\circ}$ . The chief constituent of the oil is dextro-limonene. Ciamician and Silber<sup>1</sup> examined the high boiling fractions of the oil and found traces of palmitic acid, guaiacol and a crystalline substance of the formula  $C_{16}H_{20}O_2$ , m. p.  $66^{\circ}$  to  $67^{\circ}$ . In addition, a sesquiterpene was found, and 2 bodies, both acids, of a peculiar constitution, *sedanolic* and *sedanonic acids*, together with the lactone of the former, *sedanolide*, which appears to be the chief odorous constituent of the oil. *Sedanolic acid*  $C_{12}H_{20}O_2$  a crystalline substance, m. p.  $88^{\circ}$  to  $89^{\circ}$ , is easily converted into its lactone, *sedanolide*  $C_{12}H_{18}O_2$ . *Sedanonic acid*,  $C_{12}H_{18}O_2$  melts at  $113^{\circ}$ , and possibly occurs as an anhydride in the oil. These 2 acids are nearly related, and Ciamician and Silber consider that *sedanolic acid* is *o*-oxyamyl-tetrahydrobenzoic acid, and that *sedanonic acid* is a related ketonic acid.

Schimmel & Co.<sup>2</sup> isolated and described the sesquiterpene present in this oil, which they prepared by regenerating the hydrocarbon from its crude hydrochloride. Its characters were given as follows: b. p.  $268-272^{\circ}$ , sp. gr. 0.9196 at  $20^{\circ}$ , optical rotation  $+49^{\circ} 30'$  and ref. index 1.5048. Semmler and Risse<sup>3</sup> consider that a second sesquiterpene has been present, and that after the elimination of this pure selinene should have a rotation of  $+61^{\circ} 36'$  and a ref. index 1.5092.

### Champaca Oil.

This oil, somewhat resembling ylang-ylang oil, is one of very high perfume value. It is distilled from the flowers of *Michelia Champaca*, a plant cultivated, and also growing wild, in the forests of the Himalayas, from Nepal and Kumaon eastwards; and also in the Nilghiris and Travancore, Java and the Philippines. The flowers, which are of an exquisite odour, are not unlike a double narcissus. The essential oil distilled from the flowers is known in India as *Pand* or *Champa-ka-utter*. The oil is known as *Yellow Champaca*, whilst that from *Michelia longifolia* is known as *White Champaca*. A sample of the former distilled in Java (yellow champaca oil) was a pale yellow oil of thin consistency, resembling, in a degree, oil of orris in odour. It had a sp. gr. 0.914, and an optical rotation  $-13^{\circ} 14'$ . The oil of white champaca from the same source had a sp. gr. 0.883 to 0.897, an optical rotation  $-12^{\circ} 50'$  and ref. index 1.4470. Its odour recalled that of basil. According to Schimmel & Co., the sp. gr. of the oil from *Michelia champaca* varies from 0.907 to 0.940 and the optical rotation from  $-12^{\circ} 18'$  to  $-55^{\circ}$ .

According to Bacon<sup>4</sup> the oil deposits crystals, and on standing for a time

<sup>1</sup> Ber. 1897, 30, 492.

<sup>2</sup> Report, April, 1910, 32.

<sup>3</sup> Ber., 1912, 45, 3301.

<sup>4</sup> Philippine J. Sci., 1910, 5, 262.

becomes semi-solid. Brooks<sup>1</sup> states that the oil has a sp. gr. of 0.904 to 0.9107 at 30°/30°, ref. index 1.4640 to 1.4688, and ester value after acetylation 199. Benzyl alcohol and benzaldehyde are constituents of the oil.

The leaf oil which is prepared on a commercial scale in Java has a sp. gr. 0.922, optical rotation +12° 30', ester value about 25, and ester value after acetylation about 60 to 65.

### Clove Oil.

Clove oil has a very high ref. index, rarely falling below 1.5310 and usually reaching 1.5340.

Castor oil has recently been found as an adulterant of clove oil. This adulterant lowers the sp. gr. and the ref. index, and causes the oil, although soluble in 1.5 to 2 volumes of 70% alcohol, to become turbid on the addition of more alcohol.

From the highest boiling fractions of oil of clove stems (b. p. 143 to 155° at 9 mm.;  $\alpha_D - 21^\circ$ ;  $d^{20}_D$  0.966;  $n^{20}_D$  1.5010) F. W. Semmler and E. W. Mayer<sup>2</sup> have isolated a sesquiterpene alcohol,  $C_{15}H_{26}O$ , which they found to possess the following constants: b. p. 138 to 148° (8 mm.),  $d^{20}_D$  0.9681,  $\alpha_D - 17^\circ$ ,  $n_D$  1.5010, mol. refr. found 68.18, calc. for  $C_{15}H_{26}O$  68.07. Judging from these values the substance is a bicyclic sesquiterpene alcohol with one double bond. The chloride of the alcohol (b. p. 147 to 155° at 12 mm.;  $d^{20}_D$  0.990) when treated with alcoholic potash solution yields a hydrocarbon having the following properties: b. p. 123 to 126° (10 mm.),  $d^{20}_D$  0.9273,  $\alpha_D^{20^\circ} - 23^\circ$ ,  $n^{20}_D$  1.5024.

Clove leaf oil closely resembles clove bud oil in characters, and contains from 78 to 88% of eugenol.

### Oil of Cubebs.

The ref. index of oil of cubebs varies from 1.4935 to 1.4970.

Some spurious cubeb oil, distilled from a species of *Piper* not yet identified, has recently been found on the market. Umney and Potter<sup>3</sup> found it to have an optical rotation of about  $-14^\circ$ .

In the fractional distillation of the oil, a considerable amount should pass over between 250° and 280°. A sample having a sp. gr. 0.913, optical rotation  $-24^\circ$  and ref. index 1.4915 gave the following results on fractionation:

Below	175°	Nil.
	180°	4 %
	185°	7 %
	190°	10 %
	200°	14 %
	210°	18 %
	220°	22 %
	230°	25 %
	240°	28 %
	250°	33 %
Above	250°	67 %

<sup>1</sup> *Philippine J. Sci.*, 1911, 6, 333.

<sup>2</sup> *Ber.*, 1912, 45, 1392.

<sup>3</sup> *Chem. and Druggist*, 1912, 80, 331, 443.

The following results were obtained on cubeb oils, recently distilled by Messrs. Stafford Allen & Sons, Ltd.

Sp. gr. at 25° C.	Rotation 100 m /m.	Ref. index at 25° C.	Distillate approx. %	
			Under 250°	250° /280°
0.919	−29.4	1.4928	21.6	75.0
0.920	−29.4	1.4930	29.0	66.0
0.923	−29.1	1.4950	17.0	78.0
0.924	−28.5	1.4944	32.0	64.0
0.923	−27.2	1.4944	14.0	80.0
0.924	−27.4	1.4949	22.0	72.0
0.927	−27.2	1.4950	50.0	44.0

Cypress Leaf Oil.

The oil from the leaves of *Cupressus sempervirens* has during the past few years become very popular as a remedy for whooping-cough.

The oil contains a mixture of terpenes, a ketone resembling thujone, a sesquiterpene, cedrol, sabinol, a sesquiterpene alcohol, and esters of terpineol.

The oil has the following characters:

	German distilled	French distilled	Algerian distilled
Sp. gr.....	0.880–0.900	0.868–0.884	0.8764
Rotation.....	+4° to +18°	+12° to +31°	+22° 18'
Ref. index.....	1.4740–1.4800	1.4710–1.4760	.....
Acid value.....	1.5 to 3.0	0 to 2	.....
Ester value.....	13 to 22	3 to 14	.....
Ester value after acetylation ...	36 to 57	9 to 32	.....

Eucalyptus Oil.

Numerous new species of eucalyptus oil have been described, but as they add nothing to the commercial and little to the chemical knowledge of this oil they need no detailed descriptions.

**Estimation of Cineol.**—The resorcinol method, advocated by Schimmel & Co., has not met with universal approval (Vol. IV, p. 341). In cases where the oil is very rich in cineol, the contents of the flask set to a solid mass and no reading is possible. This is to some extent obviated by diluting the oil with an equal volume of petroleum, and making the necessary correction in reading the unabsorbed portion. There is also no doubt<sup>1</sup> that other oxygenated constituents than cineol are absorbed, and that the process is not very accurate.

Dodge,<sup>2</sup> in a communication to the 8th Inter. Con. of Appl. Chem. has suggested another method for the estimation of cineol.

<sup>1</sup> Bennett, *Chem. and Druggist*, 1908, 1, 55; *Perf. and Ess. Oil Record*, 1912, 269.  
<sup>2</sup> *J. Ind. Eng. Chem.*, 1912, 4, 259



This is based upon the familiar fact that, in the cold, cineol remains practically unattacked by potassium permanganate, whereas the remaining constituents of the oils in question (eucalyptus oil and cajuput oil) are oxidised into soluble compounds. The process is carried out as follows: 10 c.c. of the oil are placed in a narrow-necked flask, cooled with ice-water, and shaken with a gradually-added 5 to 6% solution of potassium permanganate, until the latter is present in excess. The mixture is then left standing in ice-water for from 12 to 18 hours with occasional shaking, after which the manganese peroxide which has separated is brought into solution by carefully adding sulphurous acid (or sodium hydrogen sulphite + hydrochloric acid). The unattacked oil (eucalyptol) is brought into the neck of the flask, pipetted into a graduated tube, washed with a little alkali, and estimated volumetrically. Its sp. gr. should be 0.929 to 0.930 (15°); it should be inactive, and dissolve in 3 to 5 volumes of 60% alcohol at 25°.

Bennett<sup>1</sup> has carried out a series of estimations with the following results:

	Cineol by permanganate process	Cineol by phosphoric acid process	Resorcinol process
	%	%	%
Eucalyptol.....	98	.....	.....
Oil of eucalyptus, b. p. ....	84	70	89
Oil of eucalyptus globulus.....	80	68	65
Oil of eucalyptus amygdalina.....	78	.....	.....
Oil of cajuput, good quality.....	80	52	54
Oil of cajuput, fractionated.....	70	14	17

It is evident from these experiments that, although the process may give approximate results with eucalyptol itself and with eucalyptus oils of high cineol content; it is not to be relied upon for cajuput oils or for eucalyptus oils of the amygdalina type, since these oils evidently contain constituents which are not readily oxidised by cold solution of permanganate. Further experiments are being made in order to determine to what extent terpenes and sesquiterpenes are oxidised under different conditions. The process is easily carried out, and, if it can be modified to give accurate results, it would prove a valuable addition to analytical methods for essential oils.

### Fennel Oil.

This oil is distilled from the fruit of several varieties of *Fœniculum vulgare*, which is found all over Europe except in the north and northeast, being especially common on the Mediterranean littoral; it is also found in Asia Minor, Persia, India and Japan. Two oils are recognised in commerce, the "sweet" and "bitter" oils, the former being more esteemed. The sweet fennel is said to be *Fœniculum sativum*, but this is probably only a variety of the common wild fennel. The great variability in the fruits of different

<sup>1</sup> *Perf. and Ess. Oil Record*, 1912, 295.

districts makes it necessary to fix some limits for the physical characters of the oil, which, however, may be exceeded in individual cases. The terpenes, pinene, phellandrene, dipentene and limonene, have all been detected in fennel oils, and the ketone fenchone, and anethole. All these bodies, however, may not occur in any given sample. Upon the presence of anethole the value of the oil chiefly depends and the solidifying point of the oil is therefore a fair criterion of its value, if the oil is pure. A good oil will, according to Parry, contain as much as 60% of anethole. The sp. gr. should not fall below 0.960 nor above 0.980, and the optical rotation should vary from  $+6^{\circ}$  to  $+20^{\circ}$ . The solidifying point (see *Oil of Aniseed*) should not fall below  $+5^{\circ}$ . If necessary the crystalline stearoptene may be separated and examined, but as a rule added solid bodies will alter the other characters of the oil. The above tests will guard against the abstraction of anethole, or the addition of the residue of oil from which this body has been abstracted.

### Geranium Oil.

The following are now accepted as the characters of the various types of geranium oil.

	Sp. gr.	Rotation	Ref. index	Esters
Réunion oil.....	0.888-0.896	$-7^{\circ}$ to $-14^{\circ}$	1.462-1.468	21-33 %
African oil.....	0.892-0.904	$-6^{\circ} 30'$ to $-12^{\circ}$	1.465-1.472	15-30 %
French oil.....	0.896-0.905	$-7^{\circ}$ to $-11^{\circ}$	1.463-1.469	19-28 %
Spanish oil.....	0.897-0.907	$-7^{\circ}$ to $-11^{\circ}$	1.462-1.469	27-42 %
Corsican oil.....	0.896-0.901	$-8^{\circ}$ to $-11^{\circ}$	1.461-1.471	22-27 %
German oil.....	0.906	$-16^{\circ}$	.....	28 %

By using the acetylation and formylation processes, the following results have been obtained by various observers, in regard to the percentage of total alcohols and of citronellol present in different types of geranium oil:

Oil	Total alcohols	Citronellol	Observer
African.....	69-79 %	32-43 %	Simmons
Réunion.....	69-73 %	44-51 %	Simmons
Corsican.....	69.8 %	30.3 %	Simmons
Trappe de Staouéli.....	71.5 %	27.9 %	Simmons
French.....	72.7 %	39.8 %	Umney
Algerian.....	74.1 %	32.9 %	Umney
Bourbon.....	73.0 %	44.3 %	Umney
Corsican.....	73.7 %	45.9 %	Umney
Asian.....	69-72 %	51-62 %	Umney

Artificial esters are now a common adulterant of geranium oil. Details as to the detection of these are to be found on pages 330 to 336.

Parry<sup>1</sup> has detected ethyl oxalate as an adulterant of this oil. He gives the following particulars in reference to this adulteration.

Ethyl oxalate is a colourless, somewhat aromatic, oil of sp. gr. 1.079 at

<sup>1</sup> *Perf. and Ess. Oil Record*, 1911, 83.

20°, and b. p. 186°. It appears as rather more than twice its weight of geranyl acetate, or still more of geranyl tiglate.

The oils in question had the following characters:

	Sp. gr. at 15°	Ref. index at 20°	Apparent ester value, %	Rotation
1.	0.9197	1.4703	57.5	-10° 40'
2.	0.9093	1.4702	46.0	-10° 35'
3.	0.9225	1.4634	74.0	-10° 45'

Within a few minutes of the commencement of saponification under a reflux condenser, a good crop of silky crystals appears in the flask, due to the formation of potassium oxalate which crystallises out. The saponification liquid, freed from alcohol, and filtered from the decomposed oil, contained oxalic acid which was identified by the usual tests.

In an exhaustive classification of the geranium species and their odours, the reader is referred to an elaborate article on the genus *pelargonium* by E. M. Holmes.<sup>1</sup>

### Ginger Oil.

This oil is distilled from the rhizomes of *Zingiber officinale*, a native of tropical Asia, which is cultivated in the East and West Indies, Africa, and to a small extent in Australia.

The constituents of the oil are as follows: *d*-camphene,  $\beta$ -phellandrene, cineol, citral, borneol, geraniol (?), the sesquiterpene zingiberene, and decylic aldehyde. Ginger oil has the following characters:

Sp. gr.....	0.875 to 0.886
Optical rotation.....	-28° to -50°
Acid value.....	0 to 2
Ester value.....	0 to 15
Ester value after acetylation.....	33 to 42
Ref. index.....	1.4795 to 1.4855

Ginger oil is very sparingly soluble in alcohol, requiring from 6 to 10 volumes of 95% alcohol to give even an opalescent solution. According to Thresh, the English distilled oil yields the following fractions on distillation:

	%
Below 150°.....	5
150°-200°.....	10
200°-240°.....	8
240°-265°.....	60
265°-300°.....	7
Residue.....	10

These results yield but little information, however, as decomposition goes on to a slight extent during distillation at ordinary pressures.

### Hop Oil.

This oil is distilled from the flowers of *Humulus lupulus*. It is an oil of pronounced odour of hops, and contains the following constituents: myrcene, linalol, an acid which exists in the form of esters, and which is probably

<sup>1</sup> *Perf. and Ess. Oil Record*, 1913, 239.

isononylic acid; geraniol,  $\alpha$ -caryophyllene, and  $\beta$ -caryophyllene (the two last named appear to be the true constituents of the body named *humulene* by Chapman (*Trans.*, 1895, 67, 54, 780). Genuine hop oil has the following characters:

Sp. gr.....	0.855 to 0.895
Optical rotation.....	-1° to +1°
Ref. index.....	1.4850 to 1.4925
Acid value.....	0 to 10
Ester value.....	15 to 40
Ester value after acetylation.....	about 70 to 80.

### Juniper Berry Oil.

This oil (*vide* page 345, Vol. IV) is sometimes slightly dextrorotatory (Russian oil) and is also as highly lævorotatory as -19° (Hungarian oil).

The constituents of juniper berry oil are  $\alpha$ -pinene, camphene, terpinenol, geraniol (?), borneol (?) and cadinene. Terpeneol does not appear to be present. In distilling juniper oil fractionally, the last 20% should have a ref. index of 1.4950 to 1.5120. Adulteration with much turpentine will cause this figure to be lowered.

It is to be remembered that juniper oil alters in character to a very considerable extent by keeping. Its sp. gr. rises and its solubility decreases, so that old juniper oil will not fulfill the requirements of the various Pharmacopœias.

### Lavender Oils.

The following bodies have recently been discovered in lavender oil (from *Lavendula vera*). Elze<sup>1</sup> has isolated the alcohol nerol, and the phenol, thymol; and Schimmel & Co.<sup>2</sup> have found the sesquiterpene, caryophyllene.

Improvements in the methods of distillation appear to be responsible for occasional increases in the ester values of French and the other foreign lavender oils. A sample distilled at Barrême<sup>3</sup> was found to contain 55.7% of esters, which is confirmed by Schimmel & Co.<sup>4</sup> who have found as much as 56% for oil distilled in this district. Samples distilled in Dalmatia have also been found to contain from 43 to 57%.<sup>5</sup>

The sp. gr. of genuine lavender oils will sometimes fall to 0.880, but in such cases care should be exercised in judging all the other analytical figures of such an abnormal oil. Old oils will often be found with abnormally high sp. gr., so that the age of the oil must be taken into account. For the tendency of true and spike lavender flowers to hybridise, see Birckenstock.<sup>6</sup> The hybrid plants are known as "spigouse" and "lavandin," and the oils therefrom are midway in characters between lavender and spike oils.

Two typical lavandin oils gave the following results on analysis:

<sup>1</sup> *Chem. Zeit.*, 1910, 34, 1029.

<sup>2</sup> *Report*, April, 1913, 70.

<sup>3</sup> *Perf. and Ess. Oil Record*, 1913, 4, 134.

<sup>4</sup> *Report*, October, 1913, 68.

<sup>5</sup> *Perf. and Ess. Oil Record*, 1913, 4, 153.

<sup>6</sup> *Schimmel's Report*, Oct., 1906.

	1	2
Sp. gr.....	0.9027	0.8995
Optical rotation.....	-0° 43'	-1° 35'
Ester value.....	6.23 %	9.12 %
Total alcohols.....	34.8 %	36.5 %

For the adulteration of lavender oil with artificial esters, see under "Esters" (page 330).

The following table<sup>1</sup> shows the influence of certain adulterants on lavender oil. Samples Nos. 1 and 2 are adulterated with terpinyl acetate. No. 3 was abnormal, but as shown by an examination of the oil after steam distillation, the abnormalities were due to resinification, rather than to adulteration. No. 4 was adulterated with glyceryl acetate, and No. 5 is a pure high ester oil which gave identical, or nearly identical results, when different quantities of potash were used for saponification.

Lavender oil	No. 1	2	3		4		5	
			Original oil	Dist. with steam	Original oil	Shaken once with 5 % alc.	15 c.c. seminormal potash solution	10 c.c.
$d_{18}^4$ .....	0.9007	0.8946	0.9072	0.8932	0.8992	.....	0.8913	.....
$\alpha_D$ .....	-3° 55'	-2° 34'	-5° 14'	-5° 37'	-4° 32'	.....	-8° 43'	.....
Solub. in 70 % alcohol. ....	2.5 vol.	2.5 vol.	1.9 vol.	2.2 vol.	2.5 vol.	.....	4.5 vol.	.....
Acid value.....	0.3	0.5	0.8	.....	0.5	.....	0.3	0.3
Ester value after 1 h. sap. with 10 c.c. N/2 solution.	78.4	83.3	100.5	102.5	90.0	87.0	145.7	143.4
Ester content (calc. for linalyl ac.).....	27.4 %	29.2 %	35.2 %	35.9 %	31.5 %	30.4 %	51 %	50.2 %
Ester value after 2 h. sap. with 20 c.c. 1/2 N. solution	82.7	87.6	104.2	104.6	91.9	.....	146.0	146.0
Ester value after 1 h. sap. with 10 c.c. 1/2 N. solution + 25 c.c. alc .....	69.7	77.0	99.0	100.6	91.1	.....	144.1	132.9
Difference.....	13.0	10.6	5.2	4.0	0.8	.....	1.9	13.1
Sap. value.....	78.7	83.8	101.3	102.5	90.5	.....	.....	.....
Acid value II.....	75.7	83.7	96.7	100.6	90.6	.....	.....	.....
Difference.....	3.0	0.1	4.6	1.9	.....	.....	.....	.....
Terpinyl acet. content about	5 %	4 %	} doubtful	not ascertainable		.....	.....	.....
Esters of spar. vol. acids...	not ascertainable	.....		not ascertainable		.....	.....	.....
Glyceryl ester.....	not ascertainable	.....		not asc. present		.....	.....	.....

In regard to Spanish spike lavender oil, it is to be noted that the optical rotation of the oil (as well as of the first 10% distilled) is more often than not to the left.

Commercial spike oils, especially Spanish oil, are almost bound to contain small quantities of labiate oils other than true spike oil, because it is quite impossible to separate the flowers which are to be found growing side by side with genuine *Lavandula spica*, so that a mixture of these with a small quantity of allied species is usually thrown into the still. The following are several varieties of lavender which are occasionally distilled.

The oil from *Lavandula pedunculata* has a sp. gr. 0.939 and optical rotation -45°. It contains nearly 40% of esters, in addition to cineol and pos-

<sup>1</sup> Schimmel & Co., Report, April, 1912, 86.

sibly thujone. The oil of *Lavandula Stoechas* (the "holy rosemary" of the Spaniards) resembles rosemary rather than lavender in its odour. Its sp. gr. is about 0.940. The oil of *Lavandula dentata*, of sp. gr. 0.926, also resembles rosemary, with a marked camphoraceous odour. Charabot<sup>1</sup> records the examination of a sample of Spanish lavender oil, but does not state its source. He found in it much free linalol, but only 3% of esters. Borneol was also present.

### Lemon Oil.

A favourite adulterant of lemon oil is a highly purified Greek turpentine, fortified with lemongrass citral. Greek turpentine is obtained from *Pinus halapensis*, and has the following characters:

Sp. gr.....	0.861 to 0.486
Optical rotation.....	+33° to +39°
Ref. index.....	1.4675 to 1.4705

The analytical figures for lemon oil vary considerably at different periods of the pressing, and care should be taken to examine, as far as possible, authentic samples from various districts, pressed at different times, in order to assist one in discriminating between adulterated and merely low-grade samples.

The ref. index of pure lemon oil is usually 1.4750, rarely below 1.4750 and in the writer's experience never below 1.4740.

In certain seasons the sp. gr. may rarely fall to 0.855, and where only spring lemons are used even to 0.854, and the optical rotation will sometimes be found as low as +55.

All pure lemon oil contains a small quantity of pinene, and the writer considers that Chace's method of detecting turpentine in lemon oil (Vol. IV, p. 356) must be used with considerable caution.

### Lime Oil.

This oil is obtained either by an expression process (generally by the ecuelle) or by distillation, from *Citrus limetta* (Italian) or *Citrus medica var. acida* (West Indian). The pressed oil is the superior of the two and commands a much higher price. Italian lime oil, which is expressed, not distilled, is of a brownish-yellow colour and has a characteristic fragrant odour of the fruit with a secondary odour of bergamot. Its sp. gr. varies from 0.870 to 0.875, and its rotation from +34° to +40°. It contains linalyl acetate and citral. It also contains a little free linalol, but not more than 3 or 4%. The bulk of the oil consists of the terpene limonene.

The West Indian oil, which is the usual oil of commerce, is obtained from the fruits of *Citrus medica var. acida*, whose juice contains a large quantity of citric acid. The plant is plentiful in Jamaica, Dominica and Tahiti; but the most important plantations are on the island of Montserrat, one of the Antilles. The lime harvest here lasts from September to January, and the chief product is, of course, the lime juice.

<sup>1</sup> Bull. Soc. Chim., 17, 378.

It is well known that distilled lime oil is quite different from the hand-expressed oil, the first-named oil having a disagreeable, turpentine-like odour. H. A. Tempany and N. Greenhaigh,<sup>1</sup> who have investigated the matter are of opinion that the difference is caused by the loss, during the process of distillation, of part of the lowest and highest boiling fractions. They distilled hand-expressed oils with steam, and obtained an oil with the characteristic turpentine-like odour of the distilled oil of commerce. The highest boiling fractions of the hand-expressed oil contain a blue fluorescent, crystalline body (perhaps methyl anthranilate), which is absent from the distilled oil. Moreover, limettin, which ordinarily separates out from the hand-expressed oil when it is left standing, is absent from the distilled oil. As a rule the citral-content of the distilled oil is lower than that of the hand-expressed oil. The authors found authentic samples to show the following properties:

I. Hand-expressed oils:  $d_{40}^{30}$  0.8712 to 0.8859,  $\alpha_D^{31}$  + 31.38 to 33.43°,  $n_D^{32}$  1.4789 to 1.4851, acid value 1.35 to 2.8, citral content 2.2 to 6.6%.

II. Distilled oils:  $d_{40}^{30}$  0.8540 to 0.8858,  $\alpha_D^{31}$  + 33.09 to 34.89°,  $n_D^{32}$  1.4702 to 1.4713, acid value 0.76 to 1.3 citral content 1.2 to 2.0%.

### Linaloe Oil.

The linaloe oil of ordinary commerce is distilled both in Mexico and Europe from the wood of several species of *Bursera*, chiefly from *Bursera Delpechiana* and *Bursera aloexylon*, and is in no way connected with aloe wood, as its name implies (*lignaloë*). A linaloe wood is also exported from French Guiana and Brazil, but this, known locally as *bois de rose femelle* or *licari* wood, is the product of one of the *Lauraceæ*, probably *Ocotea caudata*. Its essential oil is known as cayenne linaloe oil, or oil of Bois de Rose.

The principal odorous substance of both oils is the alcohol, linalol. In addition Mexican linaloe oil has been found to contain geraniol, linalol oxide, methyl-heptenone, a sesquiterpene, two terpenes, methyl-heptenol, terpineol, and myrcene. Cayenne linaloe oil contains also terpineol, geraniol, methyl-heptenone, methyl-heptenol, nerol, cineol, dipentene and probably myrcene.

The general characters of the two oils usually fall within the following limits:

	Mexican	Cayenne
Sp. gr.....	0.870-0.880	0.875 to 0.898
Rotation.....	-10° to -19°	+8° to -12°
Ref. index.....	1.4610-1.4630	1.4590-1.4645
Acid value.....	1-3	1-2
Ester value.....	5-9	3-20 (rarely 40-75)
Free alcohols.....	85-96 %	84-94 %
(Determined in xylene solution).		

<sup>1</sup> West Indian Bull., 1912, 12, 498.



Both oils are soluble in 2 to 3 volumes of 70% alcohol. It must be remembered that the estimation of linalol must be carried out with the modifications in the acetylation process described under the estimation of free alcohols, xylene being the best diluent.

The behaviour of the oil on fractional distillation affords a useful indication of the purity and quality of the sample, a high linalol value being indicated by a close similarity in the various fractions constituting the first 90% distilling. A typical sample distilled by the writer and Bennett, having a sp. gr. 0.882 and an optical rotation  $-11^{\circ}$ , gave the following results:

Fraction	%	Sp. gr.	Rotation	Ref. index
1	10	0.808	$-11^{\circ}$	1.4580
2	20	0.870	$-11^{\circ}30'$	1.4590
3	20	0.871	$-13^{\circ}$	1.4605
4	20	0.872	$-13^{\circ}$	1.4612
5	20	0.876	$-120^{\circ}$	1.4620
6	10	0.913	.....	1.4750

An oil known as shiu oil distilled in Formosa from a species of cinnamon (?) contains a large amount of linalol, and may be expected to become an adulterant of linaloe oil, which is largely used in perfumery, and for the manufacture of artificial perfumes.

Shiu oil, however, contains camphor, and as it is very difficult to remove the whole of this, the presence of camphor in linaloe oil may be regarded as indicative of the presence of shiu oil. Schimmel & Co.<sup>1</sup> give the following methods for its detection.

**Detection of Camphor by Means of Semi-carbazide Hydrochloride.**—25 gm. of oil, distilled by steam, are diluted with a mixture of 1 gm. of semi-carbazide hydrochloride and 1 gm. of sodium acetate in 25 c.c. of 90% alcohol. After standing for 24 hours, 1 gm. is added and the whole mass distilled by steam. The distillation-residue is slightly evaporated in a dish on the water-bath and cooled. This causes the semi-carbazone to separate out from the camphor. A little hydrazodicarbonamide (decomposition product of the semi-carbazide hydrochloride) may be found admixed with the latter. The semi-carbazone is now filtered off and dissolved in a little alcohol, the hydrazodicarbonamide remaining undissolved. When the alcohol has evaporated the camphor semi-carbazone is left; when decomposed with dilute sulphuric acid the latter should develop a clearly perceptible odour of camphor. As a rule the semi-carbazone does not melt very sharply, because the substance is still contaminated with certain other compounds which can only be removed by repeated recrystallisation, but the quantity of the substance available is often insufficient for the purpose.

So small an addition to linaloe oil as 1% of camphor can be traced by the semi-carbazide method, especially when the mixture is allowed to stand for

<sup>1</sup> *Report*, Oct., 1913, 71.

more than 24 hours. But the method is not suitable for quantitative estimation; for example, after one single treatment of a mixture of 80% linalol and 20% camphor only 11% camphor was traceable after an interval of 2 days. The method has, moreover, the great drawback of being very slow.

**Estimation of Camphor by Oxidation with Potassium Permanganate.**—Much better results were obtained by this method, which made it possible to estimate the camphor-content rapidly and with great accuracy.

The *modus operandi* is as follows: In a distilling flask of 2 litres capacity, 50 gm. of potassium permanganate and 300 c.c. of water are placed; within the course of 30 minutes, 10 gm. linaloe oil are added gradually through a dropping funnel, cooling strongly with ice. The oil is dissolved by warming it. When the action is quite completed and no further warming takes place (after about 2 hours) a further 200 c.c. of water are added and the unattacked camphor is driven over with steam.

By this method it was possible to detect the addition to linaloe oil of 1% camphor and 10% shiu oil. The manipulation can be carried out in about 4 hours, and the method is also suitable for the quantitative estimation of camphor in linaloe oils which have been adulterated with shiu oils, for which purpose it is necessary to shake out the steam-distillate several times with ether after adding common salt. The ethereal extracts are placed together and the residue is weighed after evaporating the ether.

### Orange Oil.

The presence of citral and citronellal in orange oil is doubtful, indeed, highly improbable.

The statement that oil of orange has a higher optical rotation than any other essential oil (see Vol. IV, p. 360) is inaccurate.

Jamaican orange oil is now a regular commercial article, and although it differs slightly from Sicilian oil, the two products are very nearly identical. The writer has examined samples of this Jamaican oil with the following results. A sample of sweet oil had the following characters:

Sp. gr. at 15°.....	0.850
Optical rotation.....	+98°40
Ref. index at 20°.....	1.4719

On fractionation under 12 mm. pressure, the oil gave the following fractions:

10 c.c. of rotation + 97° 30' and ref. index 1.4709
80 c.c. of rotation + 99° 20' and ref. index 1.4707
5.7 c.c. of rotation + 86° 53' and ref. index 1.4705

The total aldehydes present were found to be 1.2%.

Two other samples of West Indian orange oil which were examined under similar circumstances contained 1.3 and 1.4% of aldehydes.

Compared with Sicilian oils the above figures show no appreciable

difference, the figures being practically identical, and the aldehyde value of such oils averaging 1.3%.

### Oil of Rue.

The herb, *Ruta graveolens*, yields an essential oil characterised by its extremely low sp. gr. The oil is of a pale yellow colour and characteristic odour, and consists almost entirely (at least 90%) of methyl-nonyl-ketone,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}_9\text{H}_{19}$ , with a small amount of methyl-heptyl-ketone. The sp. gr. of the oil varies from 0.830 to 0.847, and it is usually slightly dextrorotary, from  $0^\circ$  to  $+2^\circ 30'$ . When exposed to the action of a freezing mixture the oil solidifies to a crystalline mass at  $+9^\circ$  to  $+10^\circ$ . It begins to boil at  $215^\circ$ , and is completely distilled at  $232^\circ$ . It should dissolve to a clear solution with from 2 to 3 volumes of 70% alcohol. Pure methyl-nonyl-ketone is a bluish oil, m. p.  $+15^\circ$  and b. p.  $225^\circ$ . The fluorescent substance present is the methyl ester of methyl-anthranilic acid. The characters given below are sufficient to guard against adulteration, which, however, is frequently practised, the usual adulterant being turpentine and, more rarely, petroleum, which, however, alter the constants of the oil so much as to be very easily detected. Oil of rue is not largely employed in medicine, and has occasionally been employed for illegitimate purposes.

The less important constituents of this oil are pinene, limonene, cineol, and, in Algerian oil, traces of methyl-salicylate. The following are the characters of the principal varieties of the oil.

	French	Algerian	Spanish
Sp. gr.....	0.830-0.845	0.837-0.845	0.833 to 0.848
Rotation.....	$-0^\circ 40'$ to $+2^\circ 10'$	$0^\circ$ to $+1^\circ$	$-1^\circ$ to $+1^\circ$
Ref. index.....	1.430-1.434	1.430-1.433	1.431-1.434
Solidifying point.....	$5^\circ$ to $10^\circ$	$7^\circ$ to $11^\circ$	$-2^\circ$ to $+8^\circ$

### Petitgrain Oil.

A number of parcels of petitgrain oil have been found during the last few years, having a somewhat low ester value, and a high optical rotation. This is probably due to the more or less careless selections of the material to be distilled, in which some young fruits, more mature than usual, have been included. The ester value of such oils falls to 35%, and the optical rotation rises to  $+9^\circ$ . A sample of petitgrain oil, of authentic origin, distilled in Jamaica<sup>1</sup> has been found to have a rotation  $-6^\circ 45'$ .

Terpinyl acetate has recently been found as an adulterant of this oil. The following results are obtained on the analysis of several samples of petitgrain oil so adulterated. The analyses are by the writer and by Messrs. Schimmel & Co.

<sup>1</sup> *Bull. Imp. Instit.*, 1913, 11, 437.

	1	2	3	4
$d_{18}^{\circ}$ .....	0.9019	0.8968	0.8917	0.8905
$\alpha_D$ .....	+4° 47'	+1° 40'	+2° 56'	-12° 0'
Solubility.....	5 vol. & m. 70 p.c. alc. dilute sol. opal.	3 vol. & m. 70 p.c. alc.	1 vol. & m. 80 p.c. alc. dilute sol. opal.	Any vol. 90 p.c. alc.
Acid value.....	2.3	0.3	0.5	0.5
Ester value after 1 h. sap. with 10 c.c. N/2 alkali.....	111.2	112.4	136.8	84.0
Ester content (calc. as linalyl acetate).....	38.9 p. c.	39.4 p. c.	47.9 p. c.	29.4 p. c.
Ester value after 2 h. sap. with 20 c.c. semi-normal alkali.....	119.3	121.8	138.5	89.0
Ester value after 1 h. sap. with 10 c.c. semi-normal alkali + 25 c.c. alc.	102.3	99.7	133.5	80.5
Difference.....	17.0	22.1	5.0	8.5
Sap. value.....	113.5	112.7	137.3	.....
Acid value II.....	107.6	112.4	128.4	.....
Difference.....	5.9	0.3	8.9	.....
Terpinyl acetate content about....	9 p.c.	12 p.c.	.....	.....

### Peppermint Oil.

Japanese peppermint oil has been found to contain  $\Delta'$ -menthenone, a ketone not hitherto found in essential oils.<sup>1</sup> Lævo-limonene, which Power isolated from American oil has been found by Murayama<sup>2</sup> in Japanese oil. Messrs. Schimmel & Co.<sup>3</sup> have identified *d*-ethyl-*n*-amylcarbinol as a constituent of the Japanese oil. Neo-menthol is also present in this oil.<sup>4</sup> Thoms has carried out a series of experiments on the cultivation of the Japanese plant at Dahlem near Berlin and in German South West Africa. The characters of the oils obtained are compared in the following table with those of normal Japanese distilled oil.

	Old Jap. oil (dist. in Japan)	Oil from herb grown in German S. W. Africa	Oil from herb grown at Dahlem (summer 1911)
Sp. gr.....	0.9043 (18°)	0.9032 (22°)	0.8954 (22°)
$\alpha_D$ .....	-35.25° (23°)	-35° (24°)	-34.75° (25.5°)
Acid value.....	4.05	2.99	4.01
Ester value.....	27.73	4.68	12.744
Ester value after acet.....	289.5	304.8	283.25
Esterified menthol.....	7.74	1.302 %	3.546
Free menthol.....	72.77	83.528 %	75.271
Total menthol.....	80.51	84.830 %	78.817
Sol. p.....	cannot be determined	+20 to 20.5°	+14.5°

Conversely, Shinosaki<sup>5</sup> has examined oils distilled from German and English plants grown in Japan. The following are the figures which these oils gave on analysis.

<sup>1</sup> Schimmel's Report, Oct., 1910, 97.

<sup>2</sup> J. Pharm. Chim., 1910, vii, 1, 549.

<sup>3</sup> Report, April, 1912, 103.

<sup>4</sup> Pickard and Littlebury, Trans., 1912, 101, 109.

<sup>5</sup> J. Ind. Eng. Chem., 1913, 5, 656.

Oil from	Japanese herb	German herb		English herb		German herb from Okayama
		1910	1911	1910	1911	
$d_{40}^{20}$ .....	0.8989	0.9638 (?)	0.9105	0.9228	0.9132	0.9161
$\alpha_D^{20}$ .....	-28.92°	.....	-42.25°	-52.25°	-63.60°	-18.15°
$n_D^{20}$ .....	1.4602	1.4671	1.4672	1.4717	1.4573	.....
Acid value.....	0	19.53	0	4.42	7.06	3.45
Menthyl acetate.....	6.35	24.94	11.08	26.50	13.65	8.36
Total menthol.....	69.30	85.71	66.30	66.88	75.60	58.61
Sol. in 70% alcohol at 20° } in vols.....	2.8	2.5	insol. 15	insol. 15.3		insol.

In regard to the botanical origin of the Japanese peppermint plant, differences of opinion exist. For details of these, a paper by Holmes<sup>1</sup> should be consulted.

The following details in regard to French oil of peppermint have been given by Camus.<sup>2</sup>

*Mentha piperita* does not constitute a separate species, but is a hybrid of *Mentha viridis* and *Mentha aquatica*. It may be regarded as a sterile plant, as it fruits rarely, and even then the fruit is mostly badly developed, hence the plant must be propagated by subdividing the rhizomes. Like all *Mentha* species, *Mentha piperita* is extraordinarily variable. Too add to the confusion, different varieties are cultivated in various plantations under the common denomination of "peppermint." Several varieties also occur of the original species. *Mentha piperita* embraces 2 groups; group I including the sub-species *piperita*, Briq. with numerous varieties, while group II includes the sub-species *citrata*, Briq., which under the name of "citronella" is much grown in France because of its pleasant aroma, but does not appear to be used commercially. In its internal structure *Mentha piperita* exhibits certain features midway between those of *Mentha viridis* and *Mentha aquatica*. How variable are the *Mentha*-species is shown by *Mentha viridis*, L. and *Mentha aquatica*, L.; for the authors describe no fewer than 6 varieties of the former, and as many as 8 of the latter, besides indicating many others.

The following figures are obtained from the ordinary oil, and the oil distilled from the so-called "red" peppermint, which has only recently been cultivated in France.

	Ordinary peppermint		Red peppermint	
$d_{40}^{20}$ .....	0.9191	0.9184	0.9170	0.9136
$\alpha_D^{20}$ .....	-10° 54'	-8° 2'	-16° 38'	-13° 44'
Solubility in 80% alcohol.....	1 vol. afterwards clouding	.....	1 vol. afterwards clouding	.....
Acid value.....	0.8	0.8	1.0	1.2
Ester value.....	40.5	31.7	18.9	17.5
Menthyl acetate.....	14.3%	11.2%	6.7%	6.2%
Ester value after acet.....	160.8	169.1	180.2	185.6
Total menthol.....	50.9%	53.9%	58.0%	60.0%
Free menthol.....	39.6%	45.1%	52.8%	55.1%
Proportion of menthone.....	7.3%	.....	16.8%	.....

<sup>1</sup> *Perf. and Ess. Oil Record*, 1913, 4, 32.

<sup>2</sup> *Report of Roure-Bertrand Oils*, Oct., 1911, 3.

The limits given in Vol. IV, p. 373, for French peppermint oil are too narrow; the oil may have an optical rotation up to  $-35^{\circ}$ , and an ester value equivalent to 27% of menthyl acetate. The same remark applies to Italian oils, which may have a rotation up to  $-27^{\circ}$ .

The experimental station for medicinal plants attached to the Royal Hungarian Agricultural Academy at Klausenburg-Kolozsvár has examined a series of peppermint oils distilled in Hungary.

The Hungarian peppermint oil resembles the American oil closely. The plant yields 1.17% oil, possessing the following constants:  $d_{15}^{20}$  0.90142 to 0.91918,  $\alpha_D -26.72^{\circ}$  to  $-32.38^{\circ}$ ,  $n_D^{20}$  1.4632 to 1.4760, soluble in 3 to 5 parts 70% alcohol and in its own volume of 90% alcohol. The following fractions passed over during distillation: up to  $200^{\circ}$  7.0%, 200 to  $205^{\circ}$  10.3%, 205 to  $210^{\circ}$  13.4%, 210 to  $215^{\circ}$  12.9%, 215 to  $220^{\circ}$  16.7%, 220 to  $225^{\circ}$  11.6%, 225 to  $235^{\circ}$  16.4%.

Umney<sup>1</sup> gives the following colour reaction to distinguish Japanese from other peppermint oils:

1 c.c. of the oil is heated with 0.5 grm. of a mixture of equal parts para-formaldehyde and citric acid over a water-bath. With Japanese peppermint oil there is no colouration, whereas with American, English, Italian and German oils, a purple colour develops. This new test has the advantage of being quicker than the familiar colour test with concentrated acetic acid.

### Spearmint Oil,

Nelson<sup>2</sup> has identified phellandrene as a constituent of this oil. Dihydrocuminic acetate has been found in German spearmint oil by Elze,<sup>3</sup> and Nelson (*loc. cit.*) has found dihydrocarveol acetate in American oil.

Irk<sup>4</sup> has examined Hungarian spearmint oil which had the following characters:

Sp. gr. $15^{\circ}/4^{\circ}$ .....	=	0.9375 to 0.9513
Optical rotation.....	=	$-44.4^{\circ}$ to $-49.9^{\circ}$
Ref. index.....	=	1.4899 to 1.4931
Carvone.....		62-71 %

It is soluble in its own volume of 80% alcohol.

### Pine Needle Oil,

Böcker and Hahn<sup>5</sup> have isolated a new *aldehyde*,  $C_{15}H_{20}O$ , a new *ketone*,  $C_{15}H_{24}O$ , and a third compound,  $C_8H_{14}O$ , which has been named *pumilone*, from the oil of *Pinus pumilio*.

<sup>1</sup> *Perf. and Ess. Oil Record*, 1911, 2, 275.

<sup>2</sup> U. S. Dept. Agric., Bur. Chem., Circular No. 92.

<sup>3</sup> *Chem. Zeit.*, 1910, 34, 1175.

<sup>4</sup> *Pharm. Central.*, 1911, 52, 1111.

<sup>5</sup> *J. prakt. Chem.*, 1911, 11, 83, 489.

## Rose Oil.

The determination of the relative proportions of geraniol and citronellol in otto of rose is now recognised as one of the principal analytical factors in the examination of the oil. The amount of citronellol present varies with the country of origin of the sample. In Bulgarian otto of rose it is usually about 30–33%, and any sample falling below 28% should be regarded with considerable suspicion.

The adulteration with geraniol, if the adulterant be derived from palmarosa oil is sometimes indicated by the presence of gurjun balsam oil, which has been used as an adulterant of the palmarosa oil. Much gurjun oil is indicated by a high lævorotation, and samples with this value in excess of  $-4^{\circ}$  should be carefully examined. As little as 0.5 to 1% of gurjun oil may be detected by adding 5 or 6 drops of the sample to 10 c.c. of acetic anhydride containing 5 or 6 drops of nitric acid. A distinct purple colour develops if gurjun oil be present, the depth depending on the amount of the adulterant.

In the examination of otto of rose it must be remembered that the characters vary from season to season, and there is, in the writer's opinion, no essential oil more difficult to judge than this one. An expert nose will often yield as much or more information than the analytical values.

The following notes will afford some information in regard to ottos of rose other than Bulgarian, which are now to be found on the market.

**Anatolian Otto.**—This otto may have a high m. p. varying from  $19^{\circ}$  to  $26^{\circ}$ , and a sp. gr. up to 0.8635. The following represent typical samples, the figures varying according to the stearoptene content:

Sp. gr. $30^{\circ}/15^{\circ}$ .....	0.863	Sp. gr. $30^{\circ}/15^{\circ}$ .....	0.850
Optical rotation.....	$-2^{\circ} 30'$	Optical rotation.....	$-3^{\circ}$
Ref. index at $25^{\circ}$ .....	1.4650	Ref. index at $25^{\circ}$ .....	1.4600
Ref. index, after washing...	1.4652	M. p.....	$23^{\circ}$ to $24^{\circ}$
M. p.....	$21^{\circ}$ to $22^{\circ}$	Citronellol.....	41.1%
Stearoptene content.....	15.8	Total alcohols.....	66.8%
Total alcohol, calculated as	72.8%	Stearoptene.....	18.9%
geraniol.			
Citronellol.....	36.2%		

**French Otto.**—This otto has recently become a commercial article. Very few authentic samples have been examined, but it appears to have characters which differ within wide limits, and it must, at present, be very largely judged by its odour. The sp. gr. of apparently genuine samples has been found up to 0.872, and, when distilled from white roses, down to 0.811, on account of the presence of up to 85% of stearoptene. The latter type of otto is, of course, of little value from the point of view of odour. Umney has examined a Spanish distillate and finds it to have the following characters:

Sp. gr. $30^{\circ}/15^{\circ}$ .....	0.844
Optical rotation.....	$-2$
Ref. index.....	1.4565
M. p.....	$27^{\circ}$ to $28^{\circ}$
Percentage of stearoptene.....	33.3
M. p. of separated stearoptene.....	$31-32^{\circ}$

The writer has pointed out that adulteration with alcohol may be indi-



cated by the alteration in the characters of the oil after washing it with warm water.

The following figures show the effect of such adulteration on the washed oils.

Original oil				Oil extracted with water			
	d <sub>20</sub> <sup>25</sup>	n <sub>D</sub> <sup>25</sup>	M. p.	d <sub>20</sub> <sup>25</sup>	n <sub>D</sub> <sup>25</sup>	M. p.	Geraniol content
1	0.8597	1.46318	19.6°	0.8614	1.46628	18.7°	77.4 %
2	0.8547	1.45111	20.2°	0.8622	1.46615	17.5°	68.1 %
3	0.8663	1.46565	26°	0.8678	1.46684	26.5°	77.5 %

Rosemary Oil.

The limits given in Vol. IV (p. 390) of the physical characters of this oil require slight amendment. English Rosemary oil is frequently slightly lævorotatory. The sp. gr. of genuine Dalmatian oil is sometimes as low as 0.894. The percentage of esters may be as low as 1.2% and of total borneol 9%.

The following figures were determined by the writer and Bennett<sup>1</sup> on samples distilled from plants sent to the writer, so that their authenticity is undisputed.

	1 (Spanish)	2 (French)	3 (French)
Source.....	Leaves alone	Leaves and stalks.	Leaves alone.
Sp. gr.....	0.917	0.897	0.914
Optical rotation.....	+5° 30'	-8° 30'	-3°
Esters calculated as bornyl acetate.....	3.2 %	3.0 %	3.6 %
Total borneol.....	19.7 %	10.9 %	18.5 %
Optical rotation of first 10 % (100 mm.).....	-1°	-12° 30'	-10°

No. 1 was distilled from herb collected toward the end of last summer and dried in the sun. It consisted entirely of leaves which were well developed and of a fine green colour. The yield was 0.89%.

No. 2 was distilled from stalky herb in the dried condition, collected in February. The proportion of stalks amounted to nearly 60%. Yield of oil 0.4%.

No. 3 was distilled from the same consignment as No. 2, but the stalks were separated and the leaves alone distilled. They yielded 1.09% of oil, containing a high proportion of borneol. The leaves were somewhat discoloured, probably owing to some fermentation having taken place.

The following are the results of fractionation of the above oils:

<sup>1</sup> *Chem. and Druggist*, 1906, 1, 671.

NO. 1

Fraction		Sp. gr.	Rotation	Ref. index	B. p. commencing at
	%				
1.....	10	0.884	-1°	1.4676	152°
2.....	10	0.890	-1° 10'	1.4680	156°
3.....	10	0.895	-1° 20'	1.4681	159°
4.....	10	0.902	+1°	1.4682	162°
5.....	10	0.903	+1° 20'	1.4683	163°
6.....	10	0.911	+2°	1.4686	165°
7.....	10	0.922	+2° 30'	1.4700	169°
8.....	10	0.940	+3°	1.4736	177°
Residue.....	20	Partially crystallised.....		1.4885	185°

NO. 2

Fraction		Sp. gr.	Rotation	Ref. index
	%			
1.....	10	0.874	-12° 30'	1.4660
2.....	10	0.878	-13°	1.4670
3.....	10	0.879	-13° 30'	1.4670
4.....	10	0.883	-12° 20'	1.4670
5.....	10	0.886	-11° 20'	1.4670
6.....	10	0.891	-10° 30'	1.4670
7.....	10	0.896	- 8° 30'	1.4678
8.....	10	0.909	- 5° 30'	1.4702
Residue.....	20	.....	.....	1.4859

NO. 3

Fraction.		Sp. gr.	Rotation	Ref. index
	%			
1.....	10	0.885	-10°	1.4660
2.....	10	0.888	-10°	1.4680
3.....	10	0.891	- 9° 20'	1.4685
4.....	10	0.896	- 7° 70'	1.4686
5.....	10	0.900	- 6° 70'	1.4686
6.....	10	0.909	- 4° 50'	1.4686
7.....	10	0.921	- 1°	1.4686
8.....	10	0.938	- 2°	1.4697
Residue.....	20	Partially crystallised.....		.....

Santalwood Oil.

The following is a complete list of the constituents of santalwood oil hitherto isolated:

*Isovaleric aldehyde*

*Santene*.—C<sub>9</sub>H<sub>14</sub> (sp. gr. 0.869; rotation -0°16').

*Nortricycloeksantalane*, C<sub>11</sub>H<sub>18</sub> (sp. gr. 0.913; rotation -24°).

*Santenone*.—C<sub>9</sub>H<sub>14</sub>O (m. p. 48-52°).

*Norisoborneol*.—C<sub>9</sub>H<sub>16</sub>.OH (m. p. 58-62°).

*Teresantalol*.—C<sub>10</sub>H<sub>16</sub>.OH (m. p. 112-114°).

*Nortricycloeksantalal*.—C<sub>11</sub>H<sub>16</sub>O (sp. gr. 0.997).

*Santalone*.—C<sub>11</sub>H<sub>16</sub>O (sp. gr. 0.991; rotation -62°).

*A Ketone*.—C<sub>11</sub>H<sub>16</sub>O.

*Santalene*.—C<sub>15</sub>H<sub>24</sub> (two isomers of this sesquiterpene are present).

$\alpha$ -Santalol.— $C_{15}H_{24}O$  (sp. gr. 0.9788; rotation  $+1^{\circ} 13'$ ).

$\beta$ -Santalol.— $C_{15}H_{24}O$  (sp. gr. 0.9728; rotation  $-41^{\circ} 47'$ ).

Santalal.— $C_{15}H_{22}O$ .

Teresantalic acid.— $C_{10}H_{14}O_2$ .

Santalic Acid.— $C_{15}H_{22}O_2$ .

Three samples of santalwood oil produced in Mauritius were found to have the following characters:

	Heart-wood oil		Sap-wood oil
	1	2	3
Sp. gr.....	0.979	0.982	0.981
Rotation.....	$-21^{\circ} 50'$	$-20^{\circ} 55'$	$-21^{\circ} 15'$
Ref. index.....	1.5070	1.5065	1.5067
Acid value.....	1.9	1.9	1.9
Ester value.....	5.6	5.6	5.6
Total santalol.....	96.4 %	96.4 %	95.8 %

Recent adulterations of santalwood oil are glyceryl acetate, benzyl alcohol and castor oil.

Glyceryl acetate is indicated by the high sp. gr., low rotation and high ester value, as well as by the high amount of esters which can be extracted by shaking the oil with 5% alcohol. Benzyl alcohol can be detected by fractional distillation, as it boils at about  $205^{\circ}$ . The santalol value of samples containing benzyl alcohol will usually be an impossible one—over 100%. Castor oil raises the ester value of the oil and interferes with the solubility in petroleum ether.

### Thyme Oil.

Spanish thyme oil contains from 30 to 60% of phenols, mostly carvacrol. It is often mixed with French oil to increase the lower phenol content of the latter.

In reference to oils of *origanum*, which are naturally dealt with under thyme oil, it should be noted that the various species of this plant have been described so loosely by different botanists that the mere specific name is valueless without the addition of the name of the authority. Thus there are three different species bearing the name *Origanum creticum*, and two each described as *O. hirtum*, and *O. smyrnæum*. The species from which the oil has been actually distilled and examined are as follows:

*Origanum majoranoides*—Willd.

*Origanum onites*—Linn.

*Origanum maru*—Linn.

*Origanum hirtum*—Link.

The oil from *Origanum majoranoides* Willd contains a large amount of

phenols, consisting almost entirely of carvacrol. The oil has the following characters:

Sp. gr.....	0.962 to 0.9685
Rotation.....	0° to +1°
Phenols.....	70-80 %

It is soluble in 2.5 to 3 volumes of 70% alcohol. The oil from *Origanum onites* has a sp. gr. 0.948, rotation  $-10^{\circ} 15'$ , and phenol value 68%.<sup>1</sup>

The characters of the oil of *Origanum hirtum* are doubtful, but according to recent investigations it contains thymol and no carvacrol, although Jahns in 1879<sup>2</sup> stated that this oil contained carvacrol as its chief constituent. It is probable that Jahns' oil was misdescribed. A sample examined by the Imperial Institute<sup>3</sup> had a sp. gr. 0.944, optical rotation  $+0^{\circ} 24'$ , and phenol value 66-67%. Three distillates from *Origanum hirtum albiflorum* Hassk. had the following characters:

Sp. gr.....	0.923-0.940
Rotation.....	$+0^{\circ} 6'$ to $0^{\circ} 8'$
Ref. index.....	1.4939 to 1.5044
Phenols.....	51-60 %

### Turpentine Oil.

The literature of this oil during the past few years has been very voluminous, but the greater part of it is of an academic nature and has but little bearing on the commercial oil of turpentine used in the English-speaking countries. A number of these publications are quoted for reference, only those of a practical nature being here referred to in detail.

Vèzes has, under the authority of the Executive Committee of the White Cross Congress held in Paris in 1909, suggested the following standards for commercial oil of turpentine.

Turpentine oil is the exclusive product of the aqueous distillation (distillation with water or non-superheated steam) of the turpentine derived from various species of *Pinus*. It is a colourless, often slightly yellowish or greenish, liquid, very mobile, with a characteristic odour. Under a normal pressure of 760 mm., the oil begins to boil between  $152$  and  $156^{\circ}$ ; at least 80% by weight must have passed over at  $164^{\circ}$ . The oil should be neutral or give only a faint acid reaction; the permissible acid-content, estimated with phenolphthaleïn as an indicator, must not exceed 1.5 gm. pure potassium hydroxide (KOH) for every kilogram of oil. The oil must also be free from mineral oils and, in fact, from all bodies other than those generated in the course of the aqueous distillation of turpentine. It may contain small proportions of resin-oil and colophony, resulting from the process of manufacture, but the aggregate weight of these may not exceed 2.5%.

The oil from *Pinus maritima* (France, Spain, Portugal) is lævorotatory,

<sup>1</sup> Bull. Imp. Inst., 1911, 9, 388.

<sup>2</sup> Arch. d. Pharm., 215, 1.

<sup>3</sup> Bulletin, 1911, 9, 383.

$\alpha_D -29$  to  $-33^\circ$ ;  $d_{25}^\circ$  not below 0.8575. The oil from *Pinus halepensis* (Greece, Algeria, Provence) is dextrorotatory,  $\alpha_D +38$ , to  $+41^\circ$ ;  $d_{25}^\circ$  not below 0.8550. The American oils, which are obtained from different species of *Pinus* (*P. palustris*; *P. heterophylla* and others) are partly dextro- and partly lævorotatory; the rotation is very variable, but never higher than in the European oils.  $d_{25}^\circ$  not below 0.8560.

The writer has examined two authentic samples of Greek turpentine, an oil used largely in the south of Europe, both for legitimate purposes and for adulterating essential oils, and found them to have the following characters:

	I	II
$d_{18}^\circ$ .....	0.8605	0.862
$\alpha_D$ .....	$+36^\circ 45'$	$+39^\circ$
$n_D^{20}$ .....	1.4690	1.4736
Commences to distil at.....	$156^\circ$	$156^\circ$
Fraction 156 to $160^\circ$ .....	70 %	72 %
$\alpha_D$ of 156 to $160^\circ$ fraction.....	$+37^\circ 15'$	$+40^\circ$

During the years 1911-1912 an enormous amount of adulteration of American turpentine with wood or stump turpentine was taking place. At the same time great dissatisfaction was expressed at the inferior nature of the Russian turpentine as found on the London market. The present writer was asked to examine a large number of samples with a view to attacking the unsatisfactory position of these oils in the market, and the following details are taken from two papers, "Turpentine Standards" (*Chem. and Druggist*, Aug. 24, 1912) and "Russian Oil of Turpentine" (*Chem. and Druggist*, Oct. 26, 1912) by Ernest J. Parry.

The United States Department of Agriculture last year issued suggested standards for No. 1 or "standard" turpentine as follows: Sp. gr. at  $20^\circ = 0.862$  to  $0.870$ ; ref. index at  $20^\circ = 1.4680$  to  $1.4760$ ; 95% should distil below  $170^\circ$ . On polymerisation with sulphuric acid (38 times normal) the residue should not exceed 1% and should have a ref. index of  $1.500$  to  $1.520$ . There is no particular objection to take to these figures, other than to say that a considerable amount of stump turpentine may be present in an oil complying with them.

The close similarity in physical characters between pure gum turpentine and the so-called stump turpentine, therefore, renders it necessary that some further distinctive features shall, if possible, be taken into account, and the result of the examination of a very large number of pure and adulterated samples led Parry to consider that the behaviour of the oil toward the halogen elements gives the most useful indications of admixture with wood or stump turpentine which, by the way, must be so described in America, where it is not allowed to be dealt in as "turpentine" without proper qualification.

Both the iodine and the bromine values have been recommended in this respect, but the iodine value is, in his opinion, the more useful of the two. Its value depends on the fact that the hydrocarbons and certain other bodies

present in wood turpentine—probably on account of the method of treatment adopted in its manufacture—appear to be more saturated than those present in normal turpentine, and therefore absorb less iodine to form a fully saturated compound.

The iodine value may be determined either by the Wijs or the Hübl method, the figures of course not being identical. The following processes may be used for the determination of the bromine value: (1) 1 c.c. of the oil is dissolved in 5 c.c. of chloroform, and a 3% aqueous solution of bromine added with shaking until a permanent colouration remains; the strength of the bromine solution is determined in the usual manner, and the amount combining with the oil can be calculated. (2) 1 c.c. of the oil is dissolved in 50 c.c. of absolute alcohol, and 5 c.c. of hydrochloric acid added. A solution of 28 gm. of bromate of potassium and 100 gm. of bromide of potassium per litre is then added until a permanent brown colour remains for 1 minute after well shaking. The bromine absorbed is calculated for 1 c.c., which can be reduced to the proper bromine number by dividing it by the sp. gr., say 0.86.

Parry considers that the halogen absorption value of the 10% left after distillation of 90% of the sample affords very reliable information as regards the presence of wood turpentine, the iodine value for this fraction (Wijs) being about 355 for pure turpentine and only about 250 to 290 for wood turpentine. He gives the following figures for the various fractions of a pure and of adulterated oils.

	(1) Pure American turpen- tine	(2) Wood turpen- tine	(3) 5 % each (1) and (2)	(4) "Petro- leum" turpen- tine	(5) 50 % each (1) and (4)
Sp. gr.....	0.886	0.873	0.869	0.808	0.838
Ref. index.....	1.4720	1.4745	1.4737	1.4490	1.4610
Initial boiling point.....	155°	159°	157°	98°	99°
Distillate under 160°.....	74 %	61 %	68 %	48 %	62 %
Distillate under 170°.....	94 %	78 %	84 %	75 %	82 %
Bromine value.....	2.2	1.46	1.82	0.05	1.1
Iodine value (Hübl).....	372	264	321	9.0	190.5
Iodine value (Wijs).....	350	240	298	8.4	179
Iodine value of last 10 % (Hübl).....	360	251	304	9.0	184
Iodine value of last 10 % (Wijs).....	355	242	298	8.5	177
Ref. index of first 20 %.....	1.4719	1.4731	1.4728	1.448	1.4660
Ref. index of second 20 %.....	1.4700	1.4730	1.4720	1.449	1.4675
Ref. index of third 20 %.....	1.4712	1.4734	1.4722	1.4481	1.4721
Ref. index of fourth 20 %.....	1.4712	1.4732	1.4721	1.4470	1.4721
Ref. index of fifth 20 %.....	1.4781	1.4842	1.4821	1.4495	1.4735

and proposes the following limits for the characters of genuine American turpentine oil:

Sp. gr. at 15°.....	0.862 -0.870
Ref. index.....	1.4680-1.4730
Initial boiling point.....	154°-155.5°
Distillate under 160°.....	72-74.5 %
Distillate under 170°.....	95-97.5 %
Bromine value.....	1.96-2.31
Iodine value (Hübl).....	360-375
Iodine value (Wijs).....	335-350
Iodine value of last 10 % (Hübl).....	349-369

Iodine value of last 10 % (Wijs).....	350-365
Ref. index of first 20 %.....	1.4700-1.4722
Ref. index of second 20 %.....	1.4700-1.4724
Ref. index of third 20 %.....	1.4710-1.4735
Ref. index of fourth 20 %.....	1.4710-1.4740
Ref. index of fifth 20 %.....	1.4780-1.4821

The results of Parry's investigations in regard to Russian turpentine confirm the fact, which is stated by Professor Schindelmeiser of Dorpat University, that most of the Russian turpentine oil of commerce has had the early runnings removed for home consumption, later fractions being then exported.

The following figures are those of a number of Russian turpentines on the London market, and which are, subject to the fact that no large quantity can be obtained that has not had its earlier fractions removed, accepted as satisfactory:

	1	2	3	4
Initial b. p.....	157°	156°	157°	158°
Distils below 155°.....	none	none	none	none
Distils 155°-160°.....	1 %	1 %	5 %	11 %
Distils 160°-165°.....	44 %	45 %	40 %	18 %
Distils 165°-170°.....	37 %	35 %	42 %	48 %
Distils 170°-180°.....	15 %	16 %	10 %	19 %
Distils above 180°.....	3 %	3 %	3 %	4 %
Sp. gr. at 15°.....	0.863	0.8635	0.863	0.868
Ref. index at 20°.....	1.4730	1.4726	1.4725	1.4748
Optical rotation.....	+4°28'	+4°30'	+9°	+8°
Absorbed by 5 % KOH.....	nil	nil	nil	nil

A very large number of samples, however, have been even more largely deprived of their early runnings, and contain a considerable amount of hydrocarbons boiling over 180°, and also a considerable amount of acid bodies, which are absorbed by potassium hydroxide. Such samples are quite useless to the rectifier, as their redistillation must ensure the removal of the acid bodies and also of the bodies boiling over 180°, with a resulting loss which causes the rectification to be unremunerative.

The following are typical samples of this type:

	1	2	3	4
Initial b. p.....	148°	146°	146°	153°
Distils below 155°.....	2 %	3 %	5.5 %	1 %
Distils 155°-160°.....	3 %	3 %	5 %	3 %
Distils 160°-165°.....	35 %	34 %	22 %	36 %
Distils 165°-170°.....	48 %	50 %	46 %	50 %
Distils 170°-180°.....	12 %	10 %	21.5 %	10 %
Distils above 180°.....	0.868	0.8665	0.878	0.869
Sp. gr. at 15°.....	1.4762	1.4756	1.4780	1.4792
Ref. index at 20°.....	+8°	+9°	+11°	+12°45'
Optical rotation.....	6 %	8.5 %	7 %	3 %
Absorbed by KOH.....				

Parry gives the following figures for two samples of virgin crude Russian turpentine:

	I	II
Sp. gr.....	0.867	0.865
Optical rotation.....	+7°50'	+10°
Ref. index.....	1.4718	1.4736
Absorbed by 5 % KOH.....	5 %	6 %
Distilled below 155°.....	traces only	traces only
Distilled 155°-160°.....	65 %	63 %
Distilled 160°-165°.....	11 %	9 %
Distilled 165°-170°.....	13 %	15 %
Distilled 170°-180°.....	7.5 %	7 %
Distilled above 180°.....	3.5 %	6 %

From these two samples the tarry and acid bodies were removed and the rectified sample, in the case of No. I had the following characters:



Sp. gr.....	0.8646
Optical rotation.....	+8°
Ref. index.....	1.4890
Absorbed by KOH.....	none
Distils below 155°.....	68 %
Distils 155°-160°.....	none
Distils 160°-165°.....	13 %
Distils 165°-170°.....	10 %
Distils 170°-180°.....	7 %
Distils above 180°.....	2 %

For an exhaustive account of the characters and minute analysis of wood turpentine the *Bulletin of the U. S. Department of Agriculture* (No. 105, 1913) by L. F. Hawley should be consulted. On the polymerisation of turpentine by sulphuric acid see J. H. Coste,<sup>1</sup> and Eiber and Hue.<sup>2</sup> The *Bulletin of the U. S. Department of Agriculture* (No. 144, 1911) by Veitch and Donk on wood turpentine should also be consulted.

Wintergreen Oil.

True wintergreen oil is the product of the distillation of the leaves of *Gaultheria procumbens*, but the oil from the bark of *Betula lenta* is so closely identical with it that the two are used more or less indifferently, except in so far as the latter is much less expensive than the former, and so finds a larger employment. Both oils consist almost entirely of methyl salicylate, their characters being as follows:

	Gaultheria oil	Betula oil
Sp. gr.....	1.180-1.187	1.180-1.187
Ref. index.....	1.5350	1.5350
Distils between.....	218°-221°	218°-221°
Rotation.....	under-1°	0°
Methyl salicylate.....	98-99 %	98-99 %

The principal adulterant is synthetic methyl salicylate. The following colour test, although by no means absolute will give useful indications in cases of gross adulteration with synthetic methyl salicylate.<sup>3</sup>

The application of the test is as follows:

To 5 drops of oil in a test-tube add 5 drops of a 5% alcoholic solution of vanillin and 1 c.c. of alcohol. Shake well, and add 2 c.c. of concentrated sulphuric acid and mix thoroughly.

The following table indicates the results of the examination of typical samples:

	Colour produced
Oil of <i>Gaultheria procumbens</i> .....	Intense crimson.
Oil of <i>Betula lenta</i> .....	Deep blood red.
Doubtful (a).....	Reddish brown.
Doubtful (b).....	Reddish brown.
Methyl salicylate (synthetic).....	Yellow.

By this intensity of colouration there can be no question that one can see

<sup>1</sup> *Analyst*, 1910, 35, 112.  
<sup>2</sup> *Chem. Zeit.*, 1910, 34, 643, 657.  
<sup>3</sup> *Perfumery Record*, 1914, Vol. 4.

a difference between oils that are pure and oils that are grossly adulterated, but whether it can be made into an accurate colorimetric test is, of course, difficult to say.

. If traces of chlorine are found in the oil (see under Oil of Almonds) a crude artificial methyl salicylate must have been used as the adulterant.

American Wormseed Oil.

E. K. Nelson<sup>1</sup> has published an exhaustive investigation on the constitution of ascaridol, which appears to be the active constituent of this oil.

The hitherto isolated constituents are *p*-cymene, sylvestrene, *d*-camphor and ascaridol. The oil has the following characters:

Sp. gr.....	0.965-0.990
Optical rotation.....	-4° to -8° 50'
It is soluble in 3 vol. of 70 % alcohol.	

Ylang-ylang Oil.

The tree whose flowers yield this much valued oil is *Cananga odorata*, which grows to perfection in the Philippine Islands, more especially in Manila. The oil produced in Java and the neighbourhood is of far less value and is known as Cananga oil. The reason for the difference between these two commercial varieties is still doubtful, as there is every reason to believe that the tree is identical in both cases.

The constituents of the oil so far identified are as follows: linalol, geraniol, cadinene, *paracresol* methyl ether, benzoic and acetic esters, pinene, eugenol methyl ether, isoeugenol, methyl salicylate, and benzyl esters. Formic acid esters, safrole, isosafrole, nerol and farnesol are also probably present in the oil.

The physical characters of the oil vary within very wide limits and organoleptic tests are very necessary in its valuation. The two oils have the following characters:

	Manila	Madagascar	Bourbon
Sp. gr.....	0.922-0.970	0.960-0.981	0.960-0.975
Rotation.....	-27° to -52°	-30° to -42°	-35° to -43°
Ref. index.....	1.491-1.506	1.496-1.513	1.499-1.515
Ester value.....	75-155	110-175	131-162
Non-volatile (2 hours at 212°F.).....	4-16.5 %	15-30 %	22-43 %

Cananga Oils.

Sp. gr.....	0.900-0.950
Rotation.....	-17°-55°
Ref. index.....	1.4950-1.5110
Ester value.....	30-100

These oils should be soluble, with at most slight opalescence in 0.5 to 2 volumes of 90% alcohol, becoming turbid by further addition of alcohol.

<sup>1</sup> *J. Amer. Chem. Soc.*, 1913, 35, 84.

Petroleum oil is a common adulterant of cananga oil and will, apart from altering the physical character above quoted, decrease the solubility. Benzyl benzoate will be indicated by a high fixed residue on the water-bath after 2 hours heating.

In a communication to the *Philippine J. Sci.*, in 1908, R. F. Bacon, who has studied the production of ylang-ylang oil in Manila in much detail, and has himself superintended the distillation of certain of the samples upon which he reports, gave as the figures from his examinations the following:

	First quality	Second quality
Sp. gr. 30°/40° .....	0.911-0.958	0.896-0.942
Optical rotation (30°).....	-27° to -49°	-27° to -87°
Ref. index (30°).....	1.4747-1.4940	1.4788-1.5082
Ester number.....	90-138	42-94

At a later date, in a communication to the same journal he confirmed his classification, and presented figures for the examination of a further number of oils. He gave as limits for first and second grade oils the following:

	First quality	Second quality
Sp. gr. 30°/40°.....	0.910-0.945	0.905-0.925
	(mostly 0.920-0.920)	(mostly 0.910-0.915)
Optical rotation.....	-22° to -50°	-38° to 79°
	(mostly -40° to -50°)	(very irregular).
Ref. index.....	1.4863-1.4944	1.4910-1.5030
Ester number.....	92-129	71-88
	(average 104)	(average 81)
Ester number after acetylation...	154-214	96-141
	(average 182)	(average 118)

#### ERRATA IN VOL. IV.

Title pages, ii, iii and viii, for "Ernest C. Parry" read "Ernest J. Parry".

Pages 312 and 313, in several places, "anethol" should read "anethole."

Page 314, line 15 from bottom, "safrol," should read "safrole."

Page 358, lines 16 and 17 should be deleted. Line 18 "Solway" should read "Salway;" and insert after "2037," see also, *Trans. Chem. Soc.*, 1908, 93, 1653."

Page 359, line 9, for " $C_{11}H_{12}O_8$ " read " $C_{12}H_{14}O_8$ " and add after "myristian," line 10, "see Power and Salway, *Trans.*, 1907, 91, 2039 and 1908, 93, 1653.

Page 369, line 1 below table, for "apiol" read "apiole."

Page 389, line 9 from bottom, for "Schimmell" read "Schimmel."

Page 429, line 18, for "safrol" read "safrole."

Page 433, in last column of table "anethol" should read "anethole" and "safrol" should read "safrole."

Page 434, under *Asarum Europaeum*, it should be noted that asarol has been shown to be identical with *d*-linalol (Power and Lees, *Trans.*, 1902, 91, 63).

Page 445, In table under "Hedeoma," delete in last column "Hedeomol, pulegone" and replace by "See page 377." Under "Hop Oil" add in last column, "For later work, see "Chapman, *Trans.*, 1903, 93, 505."

Page 450, last column, insert "see however page 358 for latest work.

Page 460, in table, for "anethol" read "anethole."

Page 461, in table, for "safrol" read "safrole."

In index page 463 under "acid value" for "Dieterick" read "Dieterich." For "chironolic acid" read "chironolic acid." For "chrysanthenum" read "chrysanthemum."

Page 464 for "Dieterick" read "Dieterich."

Page 464, for "Heany" read "Heavy," "light comphor oil" read "light camphor oil."

Page 465, for "patchonlene" read "patchoulene." "Rubler" read "rubber."

Under "Tiemann" for "cital" read "citral."

# TANNINS.

By W. P. DREAPER, F. I. C.

**Tannin Materials.**—The geographical distribution of tannin in the vegetable world has been dealt with by J. Dekker.<sup>1</sup> Although the number of plants containing tannin is relatively small this substance appears in all the groups or subdivisions adopted by botanists. Algæ, fungi, and lichens often contain it, but the mass of raw material available in such cases is not sufficient to have any commercial value. Very few of the mosses give a positive indication for tannin. Many of the ferns contain tannin, from mere traces to 10%, but it is in the higher group of seed plants that tannin occurs abundantly from a commercial point of view. Among the *Gymnosperms* a number of plants contain tannin, notably the pine, hemlock, spruce and fir. The *Dicotyledons* furnish the largest number of plants rich in tannin. Several of this order are widely distributed from the tropics to the limits of vegetation. The ones used in commerce are chiefly tropical. Thus the *Combretaceæ*, consisting of about 240 tropical species, yield from one of them the myrabolans of commerce. The *Rhizophoraceæ* yield the mangrove bark. The *Leguminosæ* which are chiefly useful are also tropical such as the wattle, algarobilla, ratanhia, kino, and divi-divi. Generally speaking the chief commercial sources of tannin are found between the parallels of 30° North and South latitude, an exception is found in the *Fagaceæ* which contain the oaks and chestnuts.

Nature of material	Percentage of tannin
Mangrove bark, African.....	28.4
Mangrove bark, East African.....	28-42
Mimosa Bark, Australian.....	30
Mimosa bark, S. African.....	35-40
Mimosa bark, Paraguay.....	22-23
Quebracho Wood, Argentine.....	18.7
Algarobilla pods, Chilian.....	45.4
Myrabolans.....	29.3
Myrabolans another sample.....	38-40
Valonia.....	31-32
Oak bark, German.....	11.2
Oak bark, Californian.....	11.4
Canaigre, Texas.....	18.6
Molle Bark, Argentine.....	14.1
Chestnut, Italian.....	7-9
Sumac, Sicilian.....	25-29
Lentiscus.....	10-15
Mexico Bark ( <i>Lysilonia Candida</i> ).....	24
Mallet Bark.....	45.7
Fir Bark.....	13-16
Knopperrn.....	34-40
Trillo.....	40
Larch bark, German.....	8-10

<sup>1</sup> De looistoffen, *Bull. Koloniaal Museum te Haarlem*, 1906, No. 35.

With the possible exceptions of sumac and canaigre, these tannin plants are not cultivated. The tannin content of several of these materials (barks, nuts and wood) is shown in the foregoing table of recent estimations by Parker, Pollak, Levi and Orthman and others, the assay being conducted by the official hide powder process. Other results will be found under different headings.

**Constitution of Tannins.**—E. Fischer<sup>1</sup> claims that gallo-tannins are acyl compounds of glucose but M. Nierenstein<sup>2</sup> does not accept this view, as the result of a further examination of the tannin of hemlock, knoppert and some other tannins which contain no sugar.

**Ellagic Acid.**—By electrolytic reduction Nierenstein and Rixon<sup>3</sup> have produced leucoellagic acid which can also be obtained from digallic acid.<sup>4</sup> It has no tanning properties. If reduction takes place at 70° instead of at ordinary temperature pentahydroxydiphenylmethyloide is produced, and at 100°, a series of hexahydroxydiphenyls.

**Tannin (gallotannic acid).**—The evidence of the composite nature of gallo-tannic acid and therefore possibly of the other tannins, is accumulating and becoming more definite. Walden<sup>5</sup> first came to this conclusion after studying the dialytic behaviour and the optical activity of the acid as prepared by different methods. Aweng<sup>6</sup> came to the same conclusion through studying the condensation products with formaldehyde and Kunz-Krause and Nierenstein have since independently confirmed this view. The acid character of gallotannic acid as expressed by the presence of free hydroxyl groups (Schiff's formula) is not accepted by many chemists, notably by Boettinger.<sup>7</sup> Paniker and Stiasny have more recently studied the question of the acid character of gallotannic acid by determining the hydron concentration of gallotannin by Bredig and Fraenkel's diazoacetic ester method.<sup>8</sup> The results obtained seem to confirm the opinion that gallotannic acid is a mixture of two or more chemical individuals, possibly closely allied.

To prepare pure gallotannic acid, the last investigators consider that the method entailing the separation of sodium gallate through its insolubility in acetic ether, is the best available. Even after salting out with sodium chloride twenty-four times, gallic acid was still present, and the method utilising the unequal distribution of the acids in ether and acetone also gave unsatisfactory results.

**Analysis of Tannins.**—Since the publication of Volume V the American Official Method of estimating Tannins has been so modified that it is necessary to redescribe it in detail.

It now stands as follows:

<sup>1</sup> *Zeit. Angew. Chem.*, 1913, 26, 547.

<sup>2</sup> *Chem. Zeit.*, 1913, 37, 1237.

<sup>3</sup> *Collegium*, 1913, 514, 53.

<sup>4</sup> *Collegium*, 1912, 202.

<sup>5</sup> *Ber.*, 1897, 30, 3151.

<sup>6</sup> *Rev. Intern. Falsific.*, 1898, 11, 29.

<sup>7</sup> *Ber.*, 1884, 17, 1503.

<sup>8</sup> *Zeit. Phys. Chem.*, 50, 202.

**OFFICIAL METHOD OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION  
(A. L. C. A.) FOR THE ANALYSIS OF VEGETABLE MATERIALS  
CONTAINING TANNIN (1914).**

**I. Raw and Spent Materials.**

(1) **Caution.**—Proper care must be taken to prevent any change in the water content of raw materials during the sampling and preliminary operations. (See "General" under Sampling.)

(2) **Preparation of Sample.**—The sample must be ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(a) The temperature used for drying samples of spent material for grinding must not exceed 60° C.

(b) Samples of raw material too wet to be ground may be dried before grinding as in (a). In this case a preliminary determination of water must be made according to (IV) on the sample as received. If the portion of the sample taken for the water determination is in pieces too large to dry properly, it is permissible to reduce these to smaller size as rapidly and with as little loss of water as possible.

(3) **Water Determination.**—10 gm. of the ground material shall be dried in the manner and for the period specified for evaporation and drying in extract analysis (see IV).

(4) **Amount of Sample to be Extracted.**—Such an amount of raw material shall be extracted as will give a solution containing as nearly as practicable 0.4 gm. tannin to 100 c.c. (not less than 0.375 or more than 0.425). Of spent materials such an amount shall be taken as will give a solution of as nearly as practicable the above concentration.

(5) **Extraction.**—Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled and a container for the material to be extracted. This container shall be provided above with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted, and provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or be delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber and that it may receive the percolate from the container. The condensation water from the condenser must be at approximately the boiling temperature when it comes in contact with the material to be extracted.

The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provision must be made for preventing any of the solid particles of the material from passing into the percolate.

(A) *Woods, Barks, and Spent Materials.*—500 c.c. of the percolate shall be collected outside in approximately 2 hours and the extraction continued with 500 c.c. for 14 hours longer by the process of continuous extraction with

reflux condenser. The applied heat shall be such as to give by condensation approximately 50 c.c. in  $1\frac{1}{2}$  hours.

(B) *Materials Other than Woods, Bark and Spent.*—Digest the material in the extractor for 1 hour with water at room temperature and then extract by collecting 2 litres of percolate outside in approximately 7 hours.

(6) *Analysis.*—The percolate shall be heated at  $80^{\circ}$  C., be cooled, made to the mark and analysed according to the official method of extracts.

## II. Analysis of Extracts.

(7) *Amount and Dilution for Analysis.*—(A) *Fluid Extracts.*—Fluid extracts shall be allowed to come to room temperature, be thoroughly mixed, and such quantity weighed for analysis as will give a solution containing as nearly as possible 0.4 gm. tannin to 100 c.c. (not less than 0.375 nor more than 0.425). Precautions must be taken to prevent loss of moisture during weighing. Dissolve the extract by washing it into a litre flask with 900 c.c. of distilled water at  $85^{\circ}$  C.

*Cooling.*—(a) The solutions prepared as above shall be cooled rapidly to  $20^{\circ}$  C. with water at a temperature of not less than  $19^{\circ}$  C., be made to the mark with water at  $20^{\circ}$  C. and the analysis proceeded with at once, or

(b) The solution shall be allowed to stand over night, the temperature of the solution not being permitted to go below  $20^{\circ}$  C., be brought to  $20^{\circ}$  C. with water at not less than  $19^{\circ}$  C., be made to the mark with water at  $20^{\circ}$  C. and the analysis proceeded with.

(B) *Solid and Powdered Extracts.*—Such an amount of solid or powdered extract as will give a solution of the strength called for under liquid extracts shall be weighed in a beaker with proper precautions to prevent change of moisture. 100 c.c. of distilled water at  $85^{\circ}$  C. shall be added to the extract and the mixture placed on the water-bath, heated and stirred until a homogeneous solution is obtained. When dissolved, the solution shall immediately be washed into a litre flask with 800 c.c. of distilled water at  $85^{\circ}$  C., be cooled, etc., as under (A) above.

NOTE.—It is permissible to make up 2-litre instead of 1-litre solutions, dissolving by washing into flask with 1,800 c.c. water at  $85^{\circ}$  C. in case of fluid extracts and 1,700 c.c. water at  $85^{\circ}$  C., in case of solid or powdered extracts.

(8) *Total Solids.*—Thoroughly mix the solutions; pipette 100 c.c. into tared dish, evaporate and dry as directed under “Evaporation and Drying.” (See IV.)

(9) *Water.*—The water content is shown by the difference between 100% and the total solids.

(10) *Soluble Solids.*—S. & S. No. 590, 15 cm. single, pleated, filter paper shall be used for the filtration.

The kaolin used shall answer the following test: 2 gm. kaolin digested with 200 c.c. of distilled water at  $20^{\circ}$  C. for 1 hour shall not give more than 1



mg. of soluble solids per 100 c.c., and shall be neutral to phenolphthalein. To 1 gm. kaolin in a beaker add sufficient solution to fill the paper, stir and pour on paper. Return the filtrate to the paper when approximately 25 c.c. has collected, repeating operation for 1 hour, being careful to transfer all kaolin to the paper. At the end of the hour remove the solution from the filter paper, disturbing the kaolin as little as possible. Bring so much as needed of the original solution to exactly 20° C. as described under (7), refill the paper with this solution and begin to collect the filtrate for evaporating and drying so soon as it comes clear. The paper must be kept full and the temperature of the solution on the filter must not fall below 20° C. nor rise above 25° C. during this part of the filtration. The temperature of the solution used for refilling the paper must be kept uniformly at 20° C. and the funnels and receiving vessels must be kept covered.

Pipette 100 c.c. of clear filtrate into tared dish; evaporate and dry as under (8).

(11) **Insolubles.**—The insoluble content is shown by the difference between the total solids and the soluble solids, and represents the matters insoluble in a solution of the concentration used under the temperature conditions prescribed.

(12) **Non-tannins.**—The hide powder used for the non-tannin determination shall be of woolly texture well delimited and shall require between 12 and 13 c.c. of  $N/10$  NaOH to neutralise 10 gm. of the absolutely dry powder.

(a) Digest the hide powder with ten times its weight of distilled water till thoroughly soaked. Add 3% of chrome alum  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ , in 3% solution, calculated on the weight of the air-dry powder. Agitate frequently for several hours and let stand over night. Squeeze and wash by digesting with four successive portions of distilled water, each portion equal in amount to fifteen times the weight of the air-dry powder taken. Each digestion shall last for 15 minutes, and the hide powder shall be squeezed to approximately 75% water after each digestion except the last, a press being used if necessary. The wet hide powder used for the analysis shall contain as nearly as possible 73% of water, not less than 71% nor more than 74%. Determine the moisture in the wet hide powder by drying approximately 20 gm. (See IV.) To such quantity of the wet hide as represents as closely as practicable 12.5 gm. (not less than 12.2 nor more than 12.8) of absolutely dry hide add 200 c.c. of the original analysis solution and shake immediately for 10 minutes in some form of mechanical shaker. Squeeze immediately through linen, add 2 gm. of kaolin (answering test described under (9)) to the detannised solution and filter through a single-folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning until clear. Pipette 100 c.c. of filtrate into a tared dish, evaporate and dry as in (8).

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Funnels and receiving vessels must be kept covered during filtration.

**Flasks** graduated to deliver 200 c.c. are recommended for measuring the analysis solution to be detannised.

(b) Digest the hide powder with the amount of water and add the amount of chrome alum in solution directed under (a).

Agitate in some form of mechanical shaker for 1 hour and proceed immediately with washing and subsequent operations as directed under (a).

**NOTE.**—In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12.5 gm. of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing as nearly as possible 73% of water. Weigh the whole amount and divide by the multiple of the 12.5 gm. of actual dry hide powder taken to obtain the weight of wet hide powder for 200 c.c. of solution.

(13) **Tannin.**—The tannin content is shown by the difference between the soluble solids and the corrected non-tannins, and represents the matters absorbable by hide under the conditions of the prescribed methods.

### III. Analysis of Liquors.

(14) **Dilution.**—Liquors shall be diluted for analysis with water at room temperature so as to give as nearly as possible 0.7 gm. solids per 100 c.c. of solution. Should a liquor be of such character as not to give a proper solution with water of room temperature it is permissible to dilute with water at 80° C. and cool rapidly as described under (7, A, a).

(15) **Total Solids.**—To be determined as in Extract Analysis.

(16) **Soluble Solids.**—To be determined as in Extract Analysis.

(17) **Insolubles.**—Determined as in Extract Analysis.

(18) **Non-tannins.**—To be determined by shaking 200 c.c. of solution with an amount of wet chromed hide powder, containing as nearly as possible 73% water, corresponding with an amount of dry hide powder shown in the following table:

Tannin range per 100 c.c.	Dry powder per 200 c.c.
0.35—0.45 gm.	9.0—11.0 gm.
0.25—0.35 gm.	6.5—9.0 gm.
0.15—0.25 gm.	4.0—6.5 gm.
0.00—0.15 gm.	0.0—0.0 gm.

Solutions to be shaken for non-tannins as in Extract Analysis and 100 c.c. evaporated as in Extract Analysis.

### IV. Temperature, Evaporation and Drying, Dishes.

(19) **Temperature.**—The temperature of the several portions of each solution pipetted for evaporating and drying, that is, the total solids, soluble solids and non-tannins must be identical at the time of pipetting.

(20) **Evaporation.**—All evaporations and dryings shall be conducted in the form of apparatus known as the “Combined Evaporator and Dryer” at a temperature not less than 98° C. The time of evaporation and drying shall be 16 hours.

(21) **Dishes.**—The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ in. diameter nor more than 3 in. in diameter.

#### V. Determination of Total Acidity of Liquors.

(17) **Reagents.**—(a) 1% solution of gelatin neutral to hæmatin. The addition of 25 c.c. of 95% alcohol per litre is recommended to prevent frothing. If the gelatin solution is alkaline, neutralise with *N*/10 acetic acid and if acid neutralise with *N*/10 sodium hydroxide.

(b) Hæmatin. A solution made by digesting hæmatin in cold neutral 95% alcohol in the proportion of 0.5 gm. of the former to 100 c.c. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) *N*/10 sodium hydroxide.

**Directions.**—To 25 c.c. of liquor in a cylinder that can be stoppered, add 50 c.c. of gelatin solution, dilute with water to 250 c.c., add 15 gm. of kaolin and shake vigorously. Allow to settle for at least 15 minutes, remove 30 c.c. of the supernatant solution dilute with 50 c.c. of water and titrate with *N*/10 sodium hydroxide using hæmatin solution as the indicator. Each c.c. *N*/10 sodium hydroxide is equivalent to 0.2% acid as acetic.

#### VI. General.

(18) When materials containing sulphite-cellulose extract are analysed, the fact that the material contains sulphite-cellulose extract shall be noted on the report.

(19) On public analytical work by members of this Association, the fact that the Official Method has been used, shall be so stated.

**The American Official Method of Sampling Tanning Materials** has also been altered to the following:

#### OFFICIAL METHODS FOR SAMPLING TANNING MATERIALS (1914).

**General.**—Extract, whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid, and in most solid extracts becomes less as the extract is exposed to the air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an exposure of a comparatively few moments may alter appreciably the amount of moisture it is apparent that the sampling in all its details should be done as

quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once in containers as nearly air tight as possible, and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of the liquor which have been kept with no preservative in them for some time do not represent the condition of the liquor when sampled.

(1) **Number of Packages to be Sampled.**—When carload lots, or less, of bags are to be sampled, 7% of the number of bags shall be sampled. When shipments of more than a carload and less than 2,000 bags are to be sampled, 20 bags shall be sampled. When shipments of more than 2,000 bags are to be sampled, 1% of the number of bags shall be sampled.

When 70, or less, barrels are to be sampled, 10% of the number of barrels shall be sampled. When from 71 to 140 barrels are to be sampled, 9% of the number of barrels shall be sampled. When from 141 to 210 barrels are to be sampled, 8% of the number of barrels shall be sampled. When from 211 to 280 barrels are to be sampled, 7% of the number of barrels shall be sampled. When from 281 to 350 barrels are to be sampled, 6% of the number of barrels shall be sampled. When from 351 to 420 barrels are to be sampled, 5% of the number of barrels shall be sampled. When from 421 to 500 barrels are to be sampled, 4% of the number of barrels shall be sampled. When more than 500 barrels are to be sampled, 3% of the number of barrels shall be sampled.

(2) **Liquid Extract in Barrels.**—The heads shall be removed from the number of barrels specified in (1), the contents of each barrel stirred until homogeneous, and a sample of equal size taken from each barrel. These subsamples shall be put together in a suitable closed container and be thoroughly mixed. From this bulk duplicate samples shall be drawn for analysis. These samples shall be preserved in air-tight glass containers, labelled with the date of sampling and such distinguishing marks as may be necessary. When a considerable period of time is likely to elapse between the sampling and the analysis, each individual sample shall be weighed when prepared and the certified weight of the sample be marked on the label.

(3) **Liquid Extract in Bulk.**—The extract shall be agitated with air, be plunged or be mixed by some other efficient means until homogeneous. Equal samples shall then be taken from different parts of the bulk, be placed in a proper container, and be thoroughly mixed and sampled as described in (2).

(4) **Liquid Extract in Tank Cars.**—The following methods are permissible:

(a) The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

(b) The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

NOTE.—As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

(c) The extract shall be sampled as follows while the car is being unloaded: A quart sample shall be taken from the discharge 3 minutes after the extract has begun to run; another quart sample shall be taken 3 minutes before the extract has all run out, and three other quart samples shall be taken at equal intervals between these two. These five samples shall be transferred to a suitable container as soon as taken, be thoroughly mixed and sampled as in (2).

(5) **Solid Extracts.**—The number of packages specified in (1) shall be selected, as nearly as practicable, of equal size. Whenever possible every  $n$ th package shall be set aside for sampling while the extract is being unloaded. When this is not possible, the packages shall be selected from as uniformly distributed parts of the bulk as possible.

Samples of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionally the outer and inner portions of the extract. These subsamples shall be placed in a clean, dry closed container. When sampling is completed, the whole composite sample shall be broken up till it will pass through a sieve of 1 in. mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of the required size shall be taken, be wrapped in paraffin paper, and be enclosed in the smallest clean, dry air-tight glass receptacles that will hold them, labelled, etc., as in (2).

Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mould holding at least two pounds. These subsamples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

(6) **Crude Tanning Materials.**—A. Shipments in bags, mats, barrels or other similar packages.

The number of packages specified in (1) shall be emptied in uniform horizontal layers in a pile on some clean surface. At least five equal samples shall be taken from top to bottom through the pile at uniformly distributed spots. These subsamples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples of not less than two quarts each shall be preserved in air-tight containers properly labelled.

When the number of packages to be sampled is so great as to make one

pile impracticable, two or more piles may be made, and the samples from the several piles properly mixed.

**B. Shipments in Bulk.**—(1) Nuts, beans, pods, ground materials, etc

Equal portions shall be taken from at least ten uniformly distributed parts of the bulk, be mixed and sampled as in "A."

(2) Barks, Wood, Etc., in Sticks.

Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through, and the sawdust thoroughly mixed and sampled as in "A."

**C. Materials Prepared for Leaching.**—Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly mixed, be reduced by mixing and quartering, and duplicate samples for analysis of at least one quart in size be preserved in air-tight containers, as in "A."

(7) **Spent Materials from Leaches.**—Samples of spent materials shall be taken from the top, middle and bottom, and in each case from the centre and outer portions of the leach. These subsamples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least one quart in size be preserved for analysis.

(8) **Tanning Liquors.**—The liquor shall be mixed by plunging or other effective means till homogeneous and then samples of at least one pint taken for analysis. The addition of 0.03% of thymol or other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When outline samples are taken from day to day and a composite sample analysed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered containers in as cool a place as possible, and kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed until homogeneous, and samples of not less than one pint each preserved for analysis.

When a sample is taken by a member of this association in accordance with the above method, it is requested that he state both upon the label of the sample submitted and upon the analysis blank, that this sample has been taken in accordance with the official method of sampling of The American Leather Chemists Association.

It would be undoubtedly wise for chemists not working within this association to follow the same method of sampling when working in America.

**Precipitation of Tannin.**—The use of fat-free casein (Kahlbaum's pure casein) has been suggested by C. W. Spiers<sup>1</sup> for separating tannin from cider. With a 0.5% solution of "pure" tannic acid, 50 c.c. of the solution was shaken with two 1-grm. quantities of casein for 15 minutes. The solution was filtered before the addition of the second portion and finally passed through

<sup>1</sup> *Collegium*, 1914, 530, 358.



barium sulphate. 5 c.c. of the solution, before and after detanning, were titrated with permanganate.

When testing the non-tans filtrate for tannin, Stiasny<sup>1</sup> has recently suggested the use of the following method: 3 c.c. of the solution is taken and 1 c.c. of a saturated salt solution and 2 drops of a 1% solution of meta-phosphoric acid added and then 2 drops of a 5% gelatin 5% salt solution.

Differences in the amount of non-tans obtained have been observed to be due to variations in the hide powder in different samples which actually conform to the official regulations. These absorb varying amounts of non-tans. Stiasny<sup>2</sup> has suggested, to meet this difficulty, that "if two hide powders gave no soluble matter on washing, and if the non-tans solution showed no reaction for tannin, the hide powder giving the higher non-tans should be regarded as correct." It must be remembered, however, that if the error is due to the relative extraction of some substance from the hide powder under the conditions existing during the extraction of the tannin and not to mere water-washing, the reverse might be the more correct procedure. The latter condition may quite possibly be partly responsible for the difference. The Levi-Orthman reagent 33 (a chromium compound), which is stated by the authors to differentiate between a tannin and sulphite-cellulose, has not been accepted unreservedly by the A. L. C. A. owing to differences in the results obtained for tannin as compared with the official method.<sup>3</sup>

A chromed gelatin is suggested to take the place of hide powder by E. Guisiana.<sup>4</sup> The gelatin is tanned in a basic chrome solution consisting of 100 gm. of chrome alum and 15 gm. of sodium carbonate to the litre of water. Thin leaves of pure white gelatin are placed in this solution for 24 hours. The gelatin is then insoluble in hot water. It is washed in water and treated with a 1% solution of ammonia and again well washed and dried between filter paper. The tanned gelatin may be kept in a flask of distilled water. For 10 c.c. of tannin solution the equivalent of 5 gm. of dry gelatin is taken. The shaking, filtration, etc., are as in the official hide powder method.

The analysis of spent bark, nuts, etc., may be illustrated in its results by following figures for oak bark as given by F. H. Small.<sup>5</sup>

	New bark %	Spent bark %
Total solids.....	24.15	9.73
Soluble.....	20.75	8.08
Non-tans.....	8.63	3.64
Tannin.....	12.12	4.44
Insoluble.....	3.4	1.65

**Laufmann's Molybdate Figure.**—In this method the tannin solution should contain 4 gm. per 250 c.c. of water. 10 c.c. of the filtered solution is

<sup>1</sup> *Collegium*, 1914, 525, 2.

<sup>2</sup> *Leath. Tr. Review*, 1912, 901.

<sup>3</sup> *J. A. L. C. A.*, 1914, 9, 41.

*J. A. L. C. A.*, 1913, 8, 143.

*J. A. L. C. A.*, 1914, 9, 33.



mixed with 10 c.c. of the reagent which is composed of equal volumes of a 10% solution of ammonium molybdate and a 15% solution of ammonium chloride. The precipitate formed is filtered off and 10 c.c. of the filtrate from which the tannin has been precipitated is evaporated to dryness (A). The precipitate on the filter paper is dissolved off with hot water, and the remaining filtrate added to the same, washing the pipette and beaker containing the same with water which is also added to the same solution. The whole is then evaporated to dryness (B). Both the residues are dried until constant weight is obtained which takes from 8–10 hours. The weight of the precipitate obtained is therefore B–A. The figure is expressed on the per cent. of the tannin obtained. For this the total solubles in 10 c.c. of the above solution is estimated in the usual manner, and the amount of tannin in the original solution (C) calculated from the non-tan figure. The molybdate figure is then obtained as follows:

$$\frac{(B-A)100}{C} = \text{Mo. figure.}$$

**Myrabolans.**—The bloom has been identified by Paessler and Hoffman<sup>1</sup> as crystalline in character and containing chebulinic acid (C<sub>23</sub>H<sub>22</sub>O<sub>19</sub> or C<sub>23</sub>H<sub>24</sub>O<sub>19</sub>). Its specific rotatory power is  $[\alpha]_D = 64.41^\circ$  for a 3% solution (water-alcohol). It is thought that the acid is present in the fruit as a glucoside, and that this is subsequently split by enzymic hydrolysis.

**Mangrove.**—The solid extract contains 12% water, 68.5% tannin and 17.3% non-tans. Unless the extract is to be used as a dye it is decolourised by blood albumin. The Queensland variety contains 39% tannin<sup>2</sup>. The Madagascar variety 43–44%; Celebes, 45–48%; E. Africa, 38–42%. As a result of a great number of analyses, made under the direction of J. Paessler, of German East African samples the following results were obtained for the tannin present:

	Lowest	Highest	Mean
<i>Rhisophora</i> .....	29.3 %	40.8 %	36.5 %
<i>Bruguiera</i> .....	24.8	42.3	35.8
<i>Coriops</i> .....	24.2	32.2	25.8
<i>Xylocarpus</i> .....	26.7	32.5	29.8

The average quantity of water present was 14%. The absence of sodium chloride in an extract precludes the presence of mangrove (Lauffmann) although its presence may be due to other causes. A new source of mangrove extract is said to be the black mangrove (*Avicennia nitida*) of the Bahama Islands.

**Cutch.**—This material is not the original cutch made in India and used in dyeing, but it is now made from a species of Borneo mangrove, the so-called

<sup>1</sup> *Lederlechn. Rundschau*, 1913, 5, 129.

<sup>2</sup> *Coombs and Russell, J. Soc. Chem. Ind.*, 1912, 31, 212.

*tengah bark* or bastard mangrove. It gives a light golden colour to leather. Its analysis is as follows:

Moisture.....	19.4 %	
Total Solids.....	80.16	
Soluble solids.....	79.10	
Insoluble.....	1.06	
Non-tannins.....	20.94	
Tannin.....	58.16	(Bachus).

**Mallet Bark (*Eucalyptus occidentalis*).**—This bark has been on the market for 8–9 years whence it came from Australia. Only the flesh of the bark is used, the *ross* being of little value. The tannin is easily soluble, 95% of it dissolving in cold water. The temperature of extraction must not exceed 60–70°. An analysis gives 38% tannin; non-tans 11% which include 1.4% dextrose and 0.8% cane sugar. The solutions keep well and give a satisfactory colour to leather.

**Chestnut-oak Bark.**—Differences in the percentage of tannin as also in the non-tans may occur in extracts prepared from new or stored bark. New bark produces more liquor of a poorer quality. The difference consists not in the amount of tannin present in the stored bark but in the greater solubility of the tannins present. The extract from the old bark being better quality.<sup>1</sup>

A comparison of thirty-three specimens of chestnut wood (14.5% H<sub>2</sub>O) gave the following great variations on analysis:

Tannin.....	8.1 to 17.2 %	(filter method)
Tannin.....	7.1 to 15.8	(shake method)
Non-tans to 100 pts. tans.....	10 to 47	(filter)
Non-tans to 100 pts. tans.....	20 to 65	(shake)

In cases where low tannin results were obtained with high non-tans the samples of bark were obtained from young wood. The results obtained from a representative wood and an extract, showed the following great differences:

	Chestnut wood		Chestnut extract	
	(filter)	(shake)	(filter)	(shake)
Tannin.....	10.0	9.2	30.0	28.5
Non-tans .....	1.7	2.5	9.5	11.0
Non-tans to 100 tans.....	17.0	27.0	32.0	39.0

The analyst must remember that the ratio of non-tans to 100 tannin will also vary greatly with the method of extraction of the wood bark or fruit. It is generally higher when extracted commercially than when extracted in the laboratory.

Differences are brought about by variations in pressure during extraction. Thus extracting for 1 hour the following results have been obtained with chestnut wood.<sup>2</sup>

<sup>1</sup> Smoot, J. A. L. C. A., 1913, 8, 1071.  
<sup>2</sup> Paessler, *Ledertechn. Rundschau.*, 1912, 361.

	1 atmos.	3 atmos.	4 atmos.	5 atmos.
Tannin (shake method).....	11.2	11.2	10.9	9.6
Non-tans.....	3.4	4.3	7.1	11.5
Tans (100) to non-tans.....	30.0	38.0	65.0	120.0

The effect of extraction under pressure in an autoclave is also seen in the following figures:

	Chestnut		Oak	
	Open	Pressure	Open	Pressure
Tannin.....	32.0%	29.8%	31.3%	26.5%
Non-tans.....	7.3	12.0	8.2	14.0
Insolubles.....	0.0	0.0	0.0	0.5
Water.....	60.7	28.5	60.5	59.0

Both these extracts stood at 25°Bé. It is said that to prevent fermentation sodium fluoride may be present up to 0.3% of the weight of extract.<sup>1</sup>

The sugars, both dextrose and cane sugar, also increase with pressure very rapidly.

Chestnut extracts are noted for their low ash which varies between 0.2 and 0.9%.

**Oak Extract.**—Results obtained with typical samples of oak extract containing 60% water were as follows (Paessler):

	Filter method	Shake method
Tannin.....	25.5–27.5%	23.0–25.0%
Non-tans.....	13.5–11.5	16.0–14.0
Dextrose.....		4.05
Cane sugar.....		2.5–1.5
100 pts. tans: Non-tans.....	42–35	56–66

For comparison with the above results oak wood itself gave the following values:

Tannin (filter).....	9.0–13.2%
Non-tans. (filter).....	4.9–6.5
Ratio 100 tans. to non-tans.....	35–54

The finished extract contains 0.6–1.3% acetic acid according to Jedlicka.<sup>2</sup> Oak Extract<sup>3</sup> owing to its high sugar content is specially liable to fermentation. It is a mixture of the pyrogallol and catechol tannins.

Emory oak occurs in the semi-arid regions of the south-western part of the United States. The bark gives 16.1% total solids; 14% solubles; 6.6% non-tans.; 7.4% tans.; 2.1% reds. On the other hand the wood itself gives total

<sup>1</sup> Thuau, *Le Cuir*, 1913, p. 595.  
<sup>2</sup> *Collegium*, 1913, 514, 33.  
<sup>3</sup> U. J. Thuau, *Le Cuir*, 1913, p. 595.

solids 8.3%; solubles 7.5%; non-tans. 4.4%; and tans 3.1%. The colour of the tannin is rather dark.

**Quebracho.**—A normal liquid extract of this wood may contain 34.5% tannin, 3.5% non-tans.; water 60%, dextrose 0.3%, cane sugar 0.2%; and ash 1.0%. An extract showing high non-tans. (6.5%) also gave a high ash (3.0%). In a special case an extract giving 28.7% tans., 10.7 non-tans., 12.2 dextrose and 2.9% ash was regarded with suspicion, and a qualitative test indicated the presence of myrabolans (Paessler). Schell<sup>1</sup> has suggested a special test to detect mangrove in quebracho extract.

The ratio of insoluble tans. to soluble ones is given by W. Moeller<sup>2</sup> as 1:10 at analysis strength. It increases at further concentration to 2:3 at 8°Bé. but on continuing the concentration to 20°Bé., solution is complete.

The adulteration of quebracho extract by mangrove may, according to van Gijn and van der Waerden,<sup>3</sup> be detected by estimating the pentoses and pentosans present in the extract by the usual Tollens-Kröber method of determining furfural. Quebracho extract is almost free from pentosans and pentoses, while mangrove contains fair quantities of these substances. Details of the method of estimation may be found in the original communication. W. Moller<sup>4</sup> criticises this method.

Lauffmann on the other hand proposes to precipitate the tannin by his ammonium molybdate method. With untreated quebracho extract the Mo-figure varies from 28 to 37, but unfortunately in sulphited quebracho this varies from 5 to 37. Mangrove extract gives a figure between 120–130 and sulphited mangrove extract 111. Stiasny<sup>5</sup> has confirmed that mixtures of these two extracts act satisfactorily with this test, but it must be noted that if a Mo-figure of 30 be taken as a standard for quebracho extract, and anything above this be regarded as due to added mangrove extract, an error equal to 20% of mangrove may be looked for if the quebracho extract is a sulphited extract giving an actual figure of 5. In making this test care must be taken to see that no pyrogallol-tans. (formaldehyde test) or sulphite cellulose (aniline test) be present. Stiasny and Wilkinson have shown that an additional sulphite process in the laboratory to equalise the original quebracho extracts to a common sulphite basis is unsatisfactory. They consider that further work will be necessary before this test can be considered as authoritative. G. A. Kerr proposes to identify the addition of mangrove by a phloroglucinol test: 100 c.c. of hydrochloric acid (12%) are placed in a 250 c.c. Erlenmeyer flask, and 2 gm. of the tannin material added in the dry state (or an equivalent amount of extract) with few pieces of pumice stone to prevent bumping. The solution is distilled through an ordinary glass condenser at the rate of 30 c.c. every 10 minutes, 30 c.c. of hydrochloric acid being added through a thistle head tube as each 30 c.c.

<sup>1</sup> *J. A. L. C. A.*, 1912, 7, 564.

<sup>2</sup> *Leadertechn. Rundschau*, 1913, 8, 258.

<sup>3</sup> *J. A. L. C. A.*, 1914, 9, 109.

<sup>4</sup> *Collegium*, 1914, 531, 85.

<sup>5</sup> *Collegium*, 1914, 526, 77.

**distil over.** Distillation is carried on until 300 c.c. have passed over. The **distillate** is tested by placing 100 c.c. in a glass beaker (2 in. diam.) and adding 8 c.c. of a solution of phloroglucinol (made by dissolving 0.25 grm. in 25 c.c. of 12% hydrochloric acid). The solution is stirred for a few moments until the colour reaches its maximum (within 5 minutes). This remains permanent for some time. With pure quebracho the colour is first a brilliant yellow, gradually becoming a bright green and finally a bluish tint as the precipitate forms, which is a dense black. With mangrove the first colour is orange, developing to a deep orange and the precipitate is buff coloured instead of black. In mixtures of quebracho and mangrove it is claimed that even so low an addition of the latter as 5% will change the colour to olive. At 50% the green colour is dominated by the orange of the mangrove. Under a low power, the precipitates may be seen side by side when small additions of mangrove are present.<sup>1</sup>

**Turwar Bark** (*Cassia Auriculata*).—The maximum tannin is extracted from this bark only at 85°–90°. No dextrose could be detected in the extract. The lead acetate precipitate has a peculiar chocolate colour.

**White Tan** (*Casalpinia Digyna*).—This is said to contain 35% of tannin and to produce a leather equal to sumac in colour. The tannin-bearing pods grow well in Burmah. The pod cases contain the tannin (Faust) to the extent of 40.07%; the non-tans. being 18.68%; insolubles 3.47% and moisture 7%.

**Sumac.**—In the detection of sumac in the state of leaf the microscopical examination of the leaf cuticle is of great value. This was originally pointed out by Lamb.<sup>2</sup> When the sumac leaves are adulterated they are generally supplied in a half or wholly ground condition, and therefore microscopical examination is necessary to disclose structure; a 1 in. objective is sufficient to detect the difference between sumac and adulterant material after the treatment recommended by Lamb. The most common adulterant is the leaves of *Pistacia Lentiscus*, which grow abundantly in Cyprus. It has even been stated that some 10,000 tons of this material are used annually to adulterate sumac. The *Tamarix Africana* is also used for this purpose. Lamb found that not more than 10% of a number of samples were unadulterated. His method of procedure is as follows: 1–2 grm. of the sample are placed in a large boiling tube and covered with nitric acid (1:1). The mixture is well shaken to thoroughly wet the sumac and the tube gently heated over a small Bunsen flame until nitrous fumes are evolved. The tube is then left to stand for 15–30 minutes. At the end of this period the tube is again heated until the solution becomes quite clear. An excess of water is then added and the mixture filtered through a close textured filter paper and the residue washed with distilled water. A small hole is then made in the filter paper and the residue washed through

<sup>1</sup> J. A. L. C. A., 1914, 9, 27.

<sup>2</sup> J. Soc. D. and Col., 1890.

into a basin with distilled water. A few drops of a solution of dyestuff added and the mixture gently warmed for a few minutes until the small particles are coloured but not so deeply as to lose their transparency. Bismarck brown, Safranine, and Methylene Blue are suitable for the purpose. After getting rid of the surplus dye solution the particles are filtered off as before through paper, washed with a little water, and a hole once more made in the filter paper and the residue washed into a clean porcelain basin. A number of the dyed particles are transferred to a microscope slide and a cover-glass placed over them. A reference to the original paper will show the considerable difference observed between the true sumac and the adulterants. The cellular structure of the adulterants is quite distinctive; the stomata afford a valuable means of identification. The treatment with nitric acid if prolonged dissolves the cuticle of sumac and leaves nothing more than what has been described as a "wreck," while the adulterants are not acted on in this manner. (See also *J. Soc. D. and Col.*, 1904. 20, 265.)

**Tannin Extracts.**—It is not possible to consider in detail the manufacture of these extracts, but the following results of analysis from different authoritative sources will serve to indicate their nature (official method of analysis):

Extract	Total solids	Insolubles	Tannin	Non-tans.
Quebracho solid, unclarified.....	88.04	7.49	74.01	6.55
Do. liquid, pure.....			30.07	5.92
Chestnut extract, liquid.....	42.95	0.35	28.45	14.15
Do.....			27.6	11.6
Oak bark liquid.....	45.8	1.47	25.3	19.03
Hemlock liquid.....	50.08	3.43	25.6	20.96
Sulphite-cellulose liquid.....	49.97	0.12	26.76	22.93

**Non-tans.**—The ratio of tans. (100) to non-tans. varies greatly according to the nature of the extract, as will be seen in the following table (Paessler). This fact may be utilised to determine the origin of an extract. At the same time the great differences which may be met with in the same extract prepared in different ways must always be remembered:

Extract	Tans.	Non-tans.	
		Filter method	Shake method
Pine bark.....	100	69	93
Oak bark.....	Do.	60	74
Sumac.....	Do.	60	74
Myrabolans.....	Do.	35	49
Divi-divi.....	Do.	41	55
Mimosa bark.....	Do.	32	39
Valonia.....	Do.	37	49
Mangrove.....	Do.	25	30
Quebracho wood.....	Do.	8	14

That the ratio of tans. to non-tans. may vary greatly in the same kind of extract is seen from the following figures (Paessler). The three extracts were chestnut extracts (25°Bé.).

Sample	Tans.		Non-tans.		Ratio tans./non-tans.	
	Filter method	Shake method	Filter method	Shake method	Filter method	Shake method
1	34.1	32.2	5.1	7.0	15	22
2	10.0	28.5	10.0	11.5	33	40
3	26.5	25.6	12.7	13.6	48	53

**Detection and Differentiation of Vegetable Tannins.**—The detection of adulteration of tannins by cheaper tannins is a matter of great difficulty to the general analyst, or even to the specialist.

**Lead Acetate Test.**—To 5 c.c. of tannin solution (analytical strength) 5 c.c. of 10% lead acetate solution are added and a portion of the clear filtrate is mixed with an excess of sodium hydroxide (10%). Mangrove, mimosa, oakwood, chestnut, myrabolans, valonia, divi-divi, algarobilla and gallic acid give colourless solutions. Quebracho and ulmo give a slight but distinct colouration, whilst *Pistacia lentiscus* and sumac give a decided yellow and wood pulp a deep yellow colouration (Stiasny).

**Acetic Acid Lead Acetate Test.**—This test has been applied quantitatively to the separation of certain tannins (Dreaper, Vol. 5, p. 70). In the following test (Stiasny) 5 c.c. of tannin solution (analytical strength) are mixed with 10 c.c. of acetic acid (10%) and 5 c.c. of lead acetate (10%) and the formation of the precipitate of lead tannate observed.

*Catechol tannins* (quebracho, mangrove, mimosa, ulmo, and gambier) give no precipitate.

*Pyrogallol tannins* (chestnut, oakwood, myrabolans, sumac, valonia, divi-divi, algarobilla, and gallo-tannic acid) give precipitates. (Note: *Pistacia lentiscus* behaves like a pyrogallol tannin in this test.) The precipitate is filtered off and the clear solution tested with a few drops of ferric alum solution (1%). Quebracho, mangrove, ulmo and gambier give a green colour, whilst mimosa, myrabolans, sumac, divi-divi, algarobilla and gallo-tannic acid give a deep bluish violet. Chestnut gives a very faint violet, whilst oakwood and valonia remain colourless. By this test it is claimed that an addition of 25% of chestnut to an oakwood extract can be detected.

**Formaldehyde Test.**—In its recent form this test is as follows: To 50 c.c. of tannin solution (analytical strength) 5 c.c. of concentrated hydrochloric acid are added and then 10 c.c. of formaldehyde (40%). The mixture is boiled in a reflux condenser for 30 minutes, cooled to the ordinary temperature and filtered. The appearance of the precipitate whilst boiling is noted and the filtrate used for the following test: To 10 c.c. of the filtrate 1 c.c. of ferric alum solution (1%) is added and about 5 grm. of solid sodium acetate, without shaking. Observe if a blue (or violet) colour appears in the lower layer. Catechol tannins are entirely precipitated by this reagent, the filtrate giving no indication with the iron salt. A portion of the pyrogallol tannins may be precipitated under this treatment, but all of them respond to the test with the iron salt. In practice this test may be



used to determine admixture of pyrogallol tannins with catechol tannins. Certain sulphated quebracho extracts (catechol) are not entirely precipitated by this reagent (Schell). After 30 minutes' boiling in the prescribed manner these special extracts are not entirely precipitated. In this case, however, and even if the filtrate be strongly coloured, it will give no distinct indication, or at least no blue colouration after the addition of the ferric alum solution and sodium acetate (Stiasny). This treatment with formaldehyde does not give a quantitative separation, as a considerable proportion of the pyrogallol tannins are co-precipitated with the catechol tannins. Small<sup>1</sup> has suggested a modified process which Stiasny thinks may give a quantitative separation.

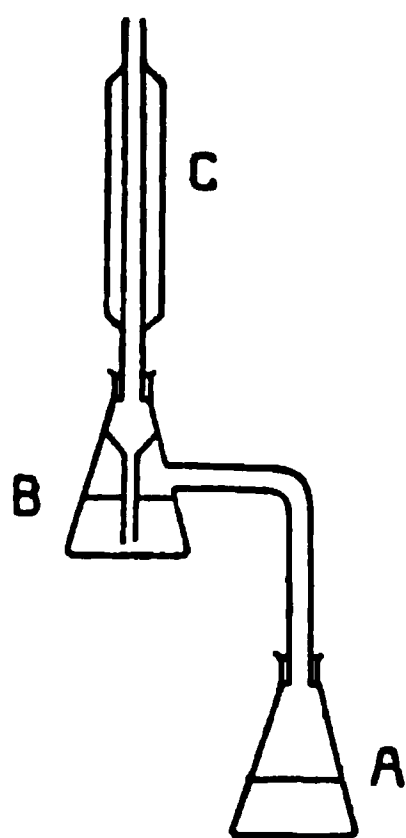


FIG. 14.

**Solubility Test.**—This test as modified by Stiasny and his pupils<sup>2</sup> is as follows: In the original test<sup>3</sup> 25 c.c. of the tannin solution were shaken out with 25 c.c. ethyl acetate until the latter remains colourless. The dry residue of the aqueous layer was compared with the total solubles of a corresponding volume of the original aqueous solution. Owing to the fact that ethyl acetate is partially soluble in water, Stiasny now suggests that it is advisable to pass a current of air for about 10 minutes through the extracted aqueous solution before taking, say, 20 c.c. for evaporation. The difference stated in percentages gives the solubility in ethyl acetate. It has been suggested that the ethyl acetate shall be replaced by amyl acetate owing to the greater insolubility of the latter in water. The test is further improved by utilising the apparatus suggested by Stiasny (Fig. 14). 50 c.c. of the amyl acetate (or ethyl acetate) are placed in flask *A* and distilled, by means of a water-bath in the case of ethyl acetate or an oil-bath in the case of amyl acetate, into the flask *B*, in such a way that the solution condensed in *C*, drops into the funnel and is forced to pass through the tannin solution in *B* before it runs back into *A*, through the side tube. With amyl acetate the flask *B* is placed in a basin with a continuous stream of cold water passing through it. The alcohol solubility figure is obtained as described in *Collegium*, 1911, 107. 10 c.c. of the solution of tannin (analytical strength) are placed in a 100 c.c. flask which is filled to the mark with absolute alcohol. 50 c.c. of the filtrate are evaporated to dryness and the weight of the dry residue compared with the total solids (solubles) of a corresponding volume of the original liquor. Reference must be made to the original communication for the figures obtained. With quebracho extract (and wood) the amyl acetate figures show 70–80% extraction by this reagent. Unfortunately sulphiting this extract greatly

<sup>1</sup> *J. A. L. C. A.*, 1911, 6, 107.<sup>2</sup> *J. A. L. C. A.*, 1912, 7, 554.<sup>3</sup> *Collegium*, 1911, 325.

reduced this figure. Complete sulphiting practically renders the tan. insoluble in amyl acetate. This greatly interferes with the validity of this test in the case of an unknown extract. Mangrove also seems to give varying results, the average extraction is about 8–10% but in one case gave 42%. The average extraction with chestnut is 10. Oakwood extract gives figures between 0–12%. It will be seen that considerable experience is necessary before this solubility test can be utilised, and then the results must be taken in conjunction with other tests. The sulphiting process practised by extract manufactures greatly interferes with the results obtained.

**Bennet's Test.**—2–3 c.c. of the tannin solution are mixed with 1 or 2 drops of a 10% solution of sodium bisulphite and an equal amount of potassium chromate. All catechol tannins are said to give a greenish colour. On the other hand, some pyrogallol tannins (myrabolans, sumac, and gallotannic acid), give a blood-red colouration which rapidly fades to brown. Other pyrogallol tannins (valonia, chestnut and oakwood extracts) give a deep violet which is fairly stable. The test is claimed to be useful for single tannins, or for subdividing the pyrogallol tannins into two subgroups. It is, however, of little value in the frequently occurring case where chestnut or oakwood is adulterated with myrabolans.

**Konstein's Test.**—The tannin is precipitated by *alcutin* (an albuminose obtained from Dr. Meyersburg, Sumper Gasse 37, Vienna) the solution filtered and a little strong ammonia added to the filtrate, which is then boiled and the change of colour observed.<sup>1</sup>

**Hoppenstedt Test.**—This is said to distinguish mangrove tannin from other extracts but can only be utilised when the mangrove extract is pure. To 25 c.c. of tannin solution (analytical strength) 25 c.c. of quinine hydrochloride (1%) solution are added and the precipitate filtered off; 1 c.c. of glacial acetic acid is added to 5 c.c. of the filtrate in a test-tube and then 5 c.c. of ethyl acetate. The liquid is mixed thoroughly by shaking and allowed to separate into layers. With mangrove the lower layer is coloured a strong yellow brown; with the other tannins the layer is colourless.

**Dieterich Test.**—This serves to detect the presence of gambier. Add 5 c.c. of alcohol to 5 c.c. of the tannin solution. After shaking add 1 c.c. of 1% potassium hydroxide solution. Then add 10 c.c. of petroleum spirit, mix, and allow the layers to separate. With gambier the upper layer exhibits a strong green fluorescence. It is claimed that this test will apply to mixtures (Hoppenstedt).

**Hoppenstedt Test for Hemlock.**—To 50 c.c. of the tannin solution add 10 grm. calcium chloride (anhydrous), agitate until dissolved, cool, and filter. 5 c.c. of the filtrate are placed in test-tube, 1 c.c. of glacial acetic acid added, then 5 c.c. of amyl acetate; shake and allow layers to separate. With hemlock the upper layer is coloured a strong yellow.

<sup>1</sup> *Collegium*, 1912, 153; see also *J. A. L. C. A.* 1912, 7, 565.

brown; with other tannins it is colourless. This is claimed to be efficient in identifying hemlock in mixtures.<sup>1</sup>

**Eitner-Philip Sulphide Test.**—This test as now given by Procter is as follows.<sup>2</sup> Add 2–3 drops of strong sulphuric acid to 25 c.c. of a strong tannin solution (2.5%) in a flask and boil for 1–2 minutes; cool, add about 5 gm. of salt, shake and allow the mixture to stand for 5–10 minutes and filter off the precipitate. In a test-tube add 10–15 drops of ammonium sulphide solution to about 15 c.c. of water and then 2–3 c.c. of the above filtrate. All pyrogallol tannins give a copious precipitate of varying colour whilst most catechol tannins give no precipitate even after standing over night. Procter (*ibid.*) states that mimosa and malet behave like pyrogallotans toward this test and that they can therefore be easily detected even in mixtures with other catechol tans. It must be remembered, however, that other tannins (pine, catechu, and gambier) are also precipitated by ammonium sulphide solution.<sup>3</sup>

Assuming that the total tannin as returned by the official method really consists of tannic acid and certain neutral substances R. Vanicek<sup>4</sup> proposes to estimate the acid in the original solution by titrating with *N*/10 sodium hydroxide, using phenolphthaleïn by the “spotting out” method. A portion of the original solution is then detannised with gelatin and the titration repeated. The difference is calculated as tannic acid, using a predetermined factor for each different tannin under examination. Stiasny considers that the values of the available tests stand in the following order:

Solubility test  
Formaldehyde test  
Acetic acid-lead acetate test  
Aniline test  
Bromine test

and that these must be taken in conjunction with the amount of tans and non-tans and their ratio and also the Löwenthal figure. There is no doubt that the latter process is coming into greater repute again and in this respect the figures given in Vol. 5 serve a useful purpose. The advent of sulphite-cellulose extracts and the fact that their active constituent is returned by the official method as tannin is one of the chief causes of the return to this process.

In extreme cases the refractometer method may be of some value and further work has been done in this direction by Kubelka.<sup>5</sup>

As has been before pointed out, when the tannin material is to be used for other purposes than that of tanning skins, the problem presented to the analyst is of a different order and this must always be remembered when deciding upon the methods to be used to estimate the tannin present. Thus in dyeing silk, the weight-giving properties of the extract in combination with its colour, alone and in the presence of mordants, are of special significance.

<sup>1</sup> *J. A. L. C. A.*, 1912, 7, 172.

<sup>2</sup> *Leather Chemist's Pocket Book*, 1912.

<sup>3</sup> *J. A. L. C. A.*, 1909, 4, 249.

<sup>4</sup> *Zeit. angew. Chem.*, 1913, 26, 68.

<sup>5</sup> *Collegium*, 1914, 527, 151.

It has been shown by Knowles<sup>1</sup> that the results obtained by the official method (A. L. T. C.) do not correspond with the results obtained on cotton with subsequent saddening with ferric sulphate, nor does the percentage of iron taken up agree with the tannin present as determined by the official method. Again in the dyeing of silk, some tannin-extracts although returning a high percentage of tannin, are quite unsuitable for certain purposes.

The chief tests for the differentiation of tannins have been conveniently collected by Stiasny in the following tables.<sup>2</sup> An interesting use is made of the formaldehyde test at both 15 and 20 minutes.

*Group I.*—Complete precipitate: the filtrate gives neither gelatin test nor iron test.

Tests for confirmation; bromine test (precipitate) and acetic acid-lead acetate test (no precipitate).

*Group II.*—No precipitation during 15 minutes' boiling.

Test for confirmation: bromine test (no precipitate); ammonium sulphide test (precipitate).

*Group III.*—Considerable precipitate during boiling, but distinct iron test of the filtrate.

To Group I belong: quebracho, mangrove, ulmo, gambier, pinebark, hemlock, mimosa, malet.

To Group II belong: oak-wood, chestnut-wood, valonia, myrabolans.

To Group III belong: oakbark, Pistacia lentiscus, sumac, divi-divi, algarobilla, teri, bablah, galls.

Having found to which group the tannin belongs, the following tests are made in each group:

Further testing of Group I.—The ammonium-sulphide test allows a subdivision, in so far as no precipitate is obtained with quebracho, mangrove, ulmo, gambier, pinebark, hemlock (Group Ia) while a precipitate is shown by minosa and malet (Group Ib).

Group Ia is also characterized by the green colouration produced with iron alum.

Group Ib gives a bluish violet with iron alum.

The further way of identifying the tannin in Ia or Ib, demands the carrying out of all the tests mentioned in previous papers and summarized in Table II. This table also contains the gallic acid value of 1 grm. of the tannin and the proportion of tans to non-tans in the tanning material. The Mo figures found by Lauffmann are also given in the table.

Further testing of Group II.—The acetic acid-lead acetate test allows a subdivision, as no colouration is given on adding iron alum to the filtrate of the lead precipitation, in the case of oak-wood and valonia (Group IIa); while a more or less distinct violet colouration is obtained with myrabolans and chestnut (Group IIb).

<sup>1</sup> J. Soc. D. and Col., 1912, 28, 174.

<sup>2</sup> J. A. L. C. A., 1914, 9, 22.

TABLE I.

50 c.c. tannin solution (0.4%) boiled with 25 c.c. of the formaldehyde-HCl mixture for 30 minutes, thoroughly cooled and filtered.

Complete precipitate: Filtrate+iron alum+sodium acetate: no violet colouration.		No precipitate after 15 minutes boiling.		Considerable precipitate after 15 minutes boiling; deep violet colouration of the filtrate+iron alum+sodium acetate.	
GROUP I		GROUP II		GROUP III	
Confirming tests: +bromine: precipitate. +acetic acid+lead acetate: no precipitate.		Confirming tests: +bromine: no precipitate. Ammonium-sulphide test: precipitate.			
25 c.c. tannin solution (2.5 %)+ammonium-sulphide test.		5 c.c. tannin solution (0.4 %)+acetic + acid lead-acetate test. The filtrate of the precipitate gives+iron alum.		5 c.c. tannin solution. (0.4 %) +bromine test.	
No precipitate.	Precipitate.	No colouration. Violet colouration.		Precipitate.	No precipitate.
GROUP Ia	GROUP Ib	GROUP IIa	GROUP IIb	GROUP IIIa	GROUP IIIb
Confirming tests: + iron alum.		Oakwood	Chestnut	Oakbark	Sumac
		Valonia	Myrabolans	Pistacia	Divi
green	bluish violet				Algarobilla
Quebracho	Mimosa				Galls
Mangrove	Malet				Bablah
Ulmo					Teri
Gambier					
Pine-bark					
Hemlock					

The sugar content of tannin extracts plays an important part in actual tanning. Apart from this the variations observed in the amounts present may also indicate the nature of the extract, and therefore be useful to the analyst.

The following table due to Paessler<sup>1</sup> indicates the differences observed when using pure extracts; the shake method was adopted for the separation of the tannin.

Material	Non-tans.	Monosaccharides	Disaccharides	Total sugars
Pine bark.....	93	33	14	47
Oak bark.....	74	30	0	30
Sumac.....	74	17	2	19
Myrabolans.....	49	18	0	18
Divi-divi.....	55	11	4	15
Mimosa.....	39	6	85	14.5
Valonia.....	49	12	0	12
Trillo.....	44	7.5	1.5	9
Mangrove.....	30	2	1	3
Quebracho wood.....	14	1	1	2

Tannin Substitutes.

A good deal of attention has been paid to these materials both as regards sulphite-cellulose products ("pseudo-tannins") and the more recently introduced synthetic tannins.

**Sulphite Cellulose Products (pseudo-tannins).**—The use of these products and their admixture with tannin extracts has drawn attention to the disturbing action of such substances on the analysis of tannin materials.

<sup>1</sup> *Collegium*, 1913, 516, 157.

TABLE II

Formaldehyde test	Bromine-test	Ammonium-sulphide test	Lead-acetate test. Filtrate + NaOH	Acetic acid + lead acetate test		Ethyl-acetate figure	Alcohol figure	Gallic acid value of 1 gm. tannin. (See College Chem., 1909, p. 191)	Tann Non-tann	Molybdenum figure (Lauffman)
					Filtrate + iron alum					
During 15 min. boiling										
No colouration	pp.	No pp.	Yellowish	No pp.	Green	70-80	0-5	0.50	8.0-10.0	25-40
No colouration	pp.	No pp.	Yellowish	No pp. (but PbSO <sub>4</sub> )	Green	0-70	0-5	0.50	Depends on the method of sulphating	0-20
No colouration	pp.	No pp.	Colourless	No pp.	Green	0-5	0-5	0.68	2.5-4.0	100-135
No colouration	pp.	No pp.	Yellowish	No pp.	Green	70-80	0-5	0.56	8.0-10.0	42
No colouration	pp.	No pp.	Colourless	No pp.	Deep bluish violet	50-65	5-10	0.56	1.5-1.5	0-13
No colouration	pp.	pp.	Colourless	No pp.	.....	30-40	0-5	0.53	8.0-3.0	110-130
Violet	pp.	pp. (after standing over night)	Colourless	pp.	.....	12	17	.....	1.0-1.5	135
No colouration	pp.	pp.	Yellowish	No pp.	Green	18	9	.....	1.0-2.0	65-85
Deep bluish violet	p.	pp.	Yellow	pp.	Green & violet	3	29	.....	.....	.....
Deep bluish violet	No pp.	pp.	Colourless	pp.	Very faint violet	0-16	10-20	0.56-0.66	8.0-3.5	180-225
Deep bluish violet	No pp.	pp.	Colourless	pp.	Colourless	0-12	20-30	0.5-0.56	1.0-2.0	175-210
Deep bluish violet.	No pp.	pp.	Colourless	pp.	Violet	30-50	0-15	0.55-0.60	1.5-2.5	80-140
Deep bluish violet	No pp.	pp.	Yellow	pp.	Violet	40-60	5-20	0.65-0.69	1.5-1.8	125-155
Deep bluish violet	No pp.	pp.	Colourless	pp.	Colourless	5-15	20-40	0.55-0.63	2.0-3.0	222
Deep bluish violet	No pp.	pp.	Colourless	pp.	Violet	30-50	0-10	.....	2	.....
Deep bluish violet	No pp.	pp.	Colourless	pp.	Violet	50-60	0-5	.....	2	.....
No colouration	No pp.	Not characteristic	Deep yellow	No pp.	Colourless	0-5	30-70	0.09-0.14	0.75	.....

The fact that sulphite extracts contain substances which are absorbed by hide powder (and are therefore returned as tannin material) is a disturbing one to the analyst who is bound to use the official methods of the European and American Associations.

Sulphite cellulose extracts give precipitates with gelatin and the alkaloïds, but fail to give the characteristic indications with other reagents used to identify tannins. As the cellulose extracts are almost always used in conjunction with normal tannin extracts and frequently mixed with them as adulterants, too much attention must not be given to the absence of certain reactions when the pure sulphite extracts are tested. They give no colour indications in the pure state with ferric salts, no red colouration with ammonia and ferrocyanide, nor any precipitate with bromine or with formaldehyde and hydrochloric acid. No precipitate is formed with tartar emetic and salt. The absence of these reactions in conjunction with a precipitate with gelatin and salt and the *apparent tannin content obtained by the hide powder process* will indicate the absence of any real tannin material and the presence of sulphite cellulose.

When treated with solvents the sulphite extracts also give certain characteristic results. Extraction with alcohol, acetone, or acetic ether, dissolves out some soluble substance, but these do not give the characteristic reactions of tannins.<sup>1</sup> Ethyl alcohol dissolves out a resinous substance insoluble in water after removing the solvent by evaporation. As previously mentioned the permanganate process of analysis gives figures "entirely outside the range of the tannins." For example a sulphite-cellulose extract giving 25% tannin by the official hide powder process only gave 5% tannin by the permanganate process. Both these processes therefore give a tannin result when no tannin is present. The analyst who is not constantly examining tannin materials should be specially careful to make sure that these products are not present in any material he is examining.

That sulphite-cellulose is undoubtedly absorbed by skins and gives a leather of sorts, and that the substances so absorbed are fairly proof against the subsequent dissolving action of water is certain. The relative weight-giving properties of these false extracts and certain tannin materials are as follows:<sup>2</sup>

Sulphite cellulose.....	100.0
Gambier.....	110.5
Sumac.....	115.1
Valonia.....	118.9
Oak bark.....	120.6
Chestnut.....	124.5
Quebracho.....	125.7

The relative cost per weight is given by the same authority to be

Sulphite cellulose.....	0.000357
Gambier.....	0.001267
Sumac.....	0.001130
Valonia.....	0.001093
Oak bark.....	0.000829
Chestnut.....	0.000498

<sup>1</sup> J. A. L. C. A., 1913, 8, 67.  
<sup>2</sup> Wisdon, J. A. L. C. A., 1913, 8, 233.



Levi and Orthmann<sup>1</sup> claim that their "reagent 33" does not give positive figures for sulphite cellulose and that therefore the process when taken in connection with the official hide powder process indicates the amount of sulphite cellulose present in an extract. Unfortunately the actual relationship between the hide powder figures and those given by reagent 33 has not been so definitely established as the authors seem to suggest. The Dreaper copper process also does not give results with sulphite cellulose extracts. (See Vol. V, p. 70.)

Eitner mentions<sup>2</sup> that the addition of these false extracts to a true extract not only cheapens the latter but improves the appearance of thick inferior quebracho extract. It has also been used as a substitute for chestnut when mixed with an addition of myrabolans, quebracho or mangrove. The ratio of the tans to non-tans by the hide powder process indicates by its variation the presence of the sulphite extracts. The sulphite extracts show a ratio of 1/0.82, whilst true vegetable tannins give figures ranging from 1/10 (quebracho) to 1/2.3 (oakwood). It has been stated that its addition to quebracho extract facilitates diffusion into the skin.

In Procter's test (previously mentioned) for the detection of these false extracts, in which to 5 c.c. of a tannin solution, 0.5 c.c. of aniline is added and after shaking 2 c.c. of concentrated hydrochloric acid, it must be noted that a slight cloudiness does not necessarily suggest adulteration. The ordinary precipitate given by sulphite extract, as compared with a clear solution with a true tannin, is of a definite nature; it is copious and after a time rises to the surface of the liquor. Certain difficulties which have arisen with this test as pointed out by Monnet<sup>3</sup> have been traced by Jedlicka<sup>4</sup> to certain pure Slavonian extracts which give a cloudiness "but that any extract may be certified as free from cellulose extracts if it does not give a flocculent precipitate after 2 hours standing." More recently the A. L. T. C. has through a committee<sup>5</sup> obtained evidence as to the reliability of this test when the above remarks are taken into consideration. An addition of 5% of sulphite cellulose was easily observed and even 2-3% could be detected in some cases.

**Synthetic Tans.**—The bodies are condensation products obtained by acting on phenols with formaldehyde.

**Neradol D.**—This artificial product which is claimed to act as a tanning material and has been put on the market by the Badische Anilin und Soda Fabrik is sent out in the form of a heavy liquid or paste of about 40° Bé. and in appearance resembles a vegetable tannin extract. It is readily soluble in water forming a clear solution of a semi-colloidal nature. According to G. Grasser<sup>6</sup> its reactions in water solution are as follows: methyl orange gives a red colouration; copper sulphate, no reaction; amm. copper sulphate, red-

<sup>1</sup> J. A. L. C. A., 1913, 8, 41.

<sup>2</sup> Gerber, 1913, 39, 43 and 57.

<sup>3</sup> Collegium, 1913, 518, 224.

<sup>4</sup> Collegium, 1913, 518, 317.

<sup>5</sup> J. A. L. T. C., 1914, 9, 36.

<sup>6</sup> J. Amer. L. T. Chem., 1913, 8, 404.

brown ppt., soluble in excess to deep brown solution; ammonia, no reaction; ferric chloride deep blue colour; lead acetate, white ppt.; gelatin, flocculent ppt.; aniline hydrochloride, heavy white ppt., basic aniline dye, ppt.; no reaction with bromine water, formaldehyde and hydrochloric acid, zinc acetate, sodium sulphite, lime water or iodine water.

Stiasny suggests the following test to distinguish between Neradol D and sulphite-cellulose: 10 c.c. of a 5% solution of the extract are shaken with 1 or 2 drops of a 1% solution of alum and about 5 grm. of ammonium acetate. On standing for 24 hours Neradol D remains clear while sulphite-cellulose gives a heavy flocculent precipitate. Neradol D is insoluble in the following solvents: ether, carbon disulphide, chloroform, acetone, and amyl alcohol. It is insoluble except its inorganic constituents, in alcohol, glacial acetic acid and acetic ether.

Analysis by the shake method gives the following results:

Water.....	34.5%
Tanning substance.....	32.5
Soluble non-tannins.....	33.0
Insolubles.....	0.0
Ash.....	17.4
The ash is composed of sodium sulphate.	

#### ERRATA IN VOL. V.

Title pages ii and iii, for "J. F. Hewitt" read "J. T. Hewitt."

Page 37, line 4, for "Silician" read "Sicilian."

Page 44, line 14, for "Proctor" read "Procter."

Page 83, lines 1 and 19, for "phlobathenes" read "phlobaphenes."

Page 103, line 7, for "*Gazetta*" read "*Gazzetta*."

Page 700, in Index, "Phlobathenes" should read "Phlobaphenes".

# ANALYSIS OF LEATHER.

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By W. P. DREAPER F. I. C.

Since this matter was treated in Vol. V, p. 105, The American Leather Chemists Association has issued the following Official Method for the analysis of leather.

## OFFICIAL METHOD FOR LEATHER ANALYSIS.

(1) **Preparation of Sample.**—The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

(2) **Moisture.**—Dry 10 gm. of leather for 16 hours at a temperature between  $95^{\circ}$ – $100^{\circ}$  C.

(3) **Fats.**—Extract 5 to 10 gm. of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below  $80^{\circ}$  C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 gm. of leather as described above. In the latter case, the extracted leather, when freed of solvent, may be used for the determination of water-soluble material.

(4) **Ash.**—Incinerate 10 to 15 gm. of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

(5) **Water-soluble Material.**—Digest 30 gm. of leather in a percolator over night, then extract with water at  $50^{\circ}$  C. for 3 hours. The total volume of solution to be 2 litres. Determine total solids and non-tannins according to the Official Method for extract analysis.

(6) **Dextrose.**

### Solutions.

**Copper Sulphate.**—Dissolve 34.639 gm. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in distilled water and dilute to 500 c.c. Filter through asbestos.

**Alkaline Tartrate Solution.**—Dissolve 173 gm. of Rochelle salt and 80 gm. NaOH in water and dilute to 500 c.c. Allow to stand two days and filter through asbestos.

**Normal Lead Acetate Solution.**—Prepare a saturated solution of normal lead acetate.

### Determination.<sup>1</sup>

Place 200 c.c. of leather extract of analytical strength in a 500 c.c. flask, add 25 c.c. of a saturated solution of normal lead acetate, shake frequently (5-10 minutes), and filter. (The funnels and beakers must be kept covered to prevent evaporation.) Add to the filtrate an excess of solid potassium oxalate. Mix frequently for 15 minutes and filter, returning the filtrate until clear. Pipette 150 c.c. of this filtrate into a 600 c.c. Erlenmeyer flask, add 5 c.c. of concentrated hydrochloric acid and boil under a reflux condenser for 2 hours. Cool, neutralise (place a small piece of litmus paper in the flask) with anhydrous sodium carbonate, transfer to a 200 c.c. graduated flask and make to volume. Filter through a double filter. (The filtrate must be clear.) Determine the dextrose in the solution immediately.

Place 25 c.c. of the copper solution and 25 c.c. of the alkaline tartrate solution in a 400 c.c. beaker. Add 50 c.c. of the clarified and neutralised solution above mentioned and heat to boiling in *exactly 4 minutes* and boil for 2 minutes. Filter immediately without diluting, *through asbestos*,<sup>2</sup> wash thoroughly, with hot<sup>2</sup> water, then with alcohol, and finally with ether; dry for half an hour in water oven and weigh as cuprous oxide, determine the amount of dextrose by the use of Munson and Walker's table (see page 415) and report as percentage on leather.

(7) Nitrogen.—Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107 (1909). (See Vol. I).

### Reagents.

**Standard Acid Solutions.**—Hydrochloric or sulphuric acid the absolute strength of which has been accurately determined. For ordinary work  $N/2$  acid is recommended. For work in determining very small amounts of nitrogen,  $N/10$  is recommended. In titrating mineral acid against hydroxide solution use cochineal as indicator.

**Standard Alkali Solution.**—The strength of this solution relative to the acid must be accurately determined;  $N/10$  solution is recommended.

**Sulphuric Acid.**—The sulphuric acid used should have a sp. gr. 1.84 and be free from nitrates and also from ammonium sulphate.

**Sodium Hydroxide Solution.**—A saturated solution of sodium hydroxide free from nitrates.

**Potassium Sulphate.**—This reagent should be pulverised before using.

**Indicator.**—A solution of cochineal is prepared by digesting and frequently agitating 3 grm. of pulverised cochineal in a mixture of 50 c.c. of

<sup>1</sup> The rate of heating of the Bunsen burner used should be regulated before sugar determinations are started. This is best done by adjusting the burner so as to bring 25 c.c. copper soln. + 25 c.c. alk. tartrate soln. + 50 c.c. water in a 400 c.c. beaker to 100°C. in exactly 4 minutes.

<sup>2</sup> The finely divided, long-fibred asbestos to be used in the glucose determination should be digested with nitric acid, washed, then digested with sodium hydroxide and washed. When gooch filters are prepared, they should be washed with boiling Fehling's solution, then with nitric acid. The mats thus prepared can be used for a long time.

strong alcohol and 200 c.c. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

### Determination.

Place 0.7 gm. of leather in a digestion flask. Add 10 gm. of powdered potassium sulphate and from 15 to 25 c.c. (ordinarily about 20 c.c.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling point of the acid from 5 to 15 minutes or until frothing has ceased (a small piece of paraffin may be added to prevent extreme foaming).

Then raise the temperature and boil briskly until the liquid has become quite clear and nearly colourless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 c.c. of water. Next add 50 c.c. of soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 c.c. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1½ hours. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

### Provisional Method of Colour Valuation of Tanning Materials.

Immerse a piece of thoroughly wetted white broadcloth, 3 by 4 in. in size, in a solution of the material to be tested containing 3% of tannin, and allow to remain with frequent agitation for 45 minutes. The solution previous to immersing the cloth is heated on a water-bath to 50° C. and the source of heat then removed, the colouring being effected without a continuance of heating. (Care must be taken that the temperature of the bath is not greater than that of the solution, *i.e.*, 50° C.) The solution, in volume 250 c.c. should be contained in a porcelain or glass beaker not less than 3½ in. in diameter and 4 in. deep, and the beaker immersed at least 2½ in. in the water. The bath should not be exposed to rapid cooling (5° being the usual drop) during the test. At the expiration of the time of immersion, the cloth is removed from the solution and the free colouring matter washed out thoroughly in water heated to 50° C., then well squeezed in the hand and further excess moisture removed by rolling for a minute or two in a clean towel. It is then dried smooth between pieces of blotting-paper in a letter press.

Newman's process of extracting the fat from fodders has been utilised by E. Golberg<sup>1</sup> for leather. Extraction takes place in the cold with tri-

<sup>1</sup> *Lederlech. Rundschau*, 1912, 49.

chlorethylene. Slightly higher results are obtained than by extraction with carbon disulphide in the Soxhlet apparatus; 10 grm. of leather are shaken with 100 c.c. of the solvent for 1 hour, and after filtering 50 c.c. are evaporated in an extraction flask to constant weight. The greatest difference between the two methods was (in one case) 0.05%.

The influence of the position of the sample taken from a hide for analysis has been emphasised by C. R. Oberfell.<sup>1</sup> Variations up to 4% in the amount of hide substance present may be obtained when samples are taken from the butt and shoulder respectively.

Under American conditions, weighting or loading leather is practised up to 16% when both glucose and Epsom salts are present. In France, leather may not be sold with an ash exceeding 1.5%. In an extended enquiry by Veitch and Rogers<sup>2</sup> it was observed that no less than 63% of the leathers examined (American) were loaded in this manner. The following particulars give in detail the results obtained: See pp. 415 to 417.

The presence of sulphite-cellulose and its detection in leather has been dealt with by W. Moeller.<sup>3</sup>

**Analysis of East Indian Tanned Hides.**—M. C. Lamb<sup>4</sup> has given many analyses indicating that on the whole these tanned hides are fairly pure. In a typical example the following results were obtained:

Leather fibre.....	68.86 %
Oil and fatty matter.....	8.43 "
Water soluble matter.....	8.6 "
Moisture.....	13.7 "
Mineral matter.....	1.12 "

Procter also estimates the insoluble residue after extraction and estimates the nitrogen in this to determine the actual hide substance present.

The nature of the tannin material in the leather is determined by Kohnstein<sup>5</sup> by boiling a portion of the water extract from the leather under a reflux condenser with formaldehyde and hydrochloric acid and filtering the solution after well cooling. The usual test with iron alum and sodium acetate will indicate the presence of pyrogallol tannin. Quebracho or mimosa tannin may be recognised by placing a drop of sulphuric acid on a rod moistened with extract when in their presence a purple colour developing to violet will be noticed.

**Chrome Leather.**—In the analysis of chrome leather which contains no tannin certain modifications are necessary. The leather may be pulverised and extracted with petroleum ether. After drying it is extracted with 90% alcohol for 3 to 4 hours. The leather is then extracted with water in the same way as ordinary leather. The petroleum ether extract contains the non-saponifiable fats and any free sulphur. Nitrogen is determined in the usual

<sup>1</sup> *J. A. L. C. A.*, 1912, 7, 127.

<sup>2</sup> *Bull. Dept. Agric. Bureau of Chemistry*, 1914.

<sup>3</sup> *Collegium*, 1914, 531, 489.

<sup>4</sup> *Tanners Year Book*, 1913, 165.

<sup>5</sup> *Allgem. Geber. Zeit.*, 1912, 14, 5.

ANALYSIS OF AMERICAN LEATHERS.

LEATHER ANALYSIS

415

Place sample was obtained	Time sample was obtained	Description of sample	Tannage claimed	Moisture, per cent.	Ash, per cent.	Petroleum ether extract, per cent.	Water-soluble material			Epsom salts, per cent.	Glucose, per cent.	Combined tannins, per cent.	Hide substance, per cent.	Ratio of combined tannins to hide substance
							Tannins, per cent.	Non-tannins, per cent.	Total soluble, per cent.					
Boston, Mass.....	1906	Sole, supposed to be weighted.	Oak.....	7.5	0.95	1.5	12.7	14.0	26.7	.....	5.4	26.1	37.9	0.69
Do.	1907	No. 1, Texas oak sole.....	Do.	6.9	0.8	4.9	17.0	6.8	23.8	.....	1.5	24.7	39.4	0.63
Do.	Do.	No. 2, Texas oak sole.....	Do.	6.5	2.1	1.7	10.2	18.9	29.1	.....	5.7	30.9	31.5	0.98
Do.	Do.	No. 3, Hemlock sole.....	Hemlock.	7.3	1.9	2.2	14.8	11.9	26.7	3.9	7.2	25.8	37.7	0.68
Do.	Do.	No. 4, Oak sole.....	Oak.....	6.9	1.2	4.0	15.1	6.4	21.5	0.5	2.6	29.2	38.1	0.77
Do.	Do.	No. 5, English pure bark.....	.....	7.3	2.3	1.3	14.2	11.3	25.5	0.7	0.7	27.0	38.6	0.70
Do.	Do.	No. 6, Hemlock sole.....	Hemlock.	7.7	1.0	1.3	17.7	11.5	29.2	1.2	4.6	24.1	37.4	0.64
Baltimore, Md....	Do.	Oak sole.....	Oak.....	6.8	2.6	1.0	14.9	18.4	33.3	4.7	12.0	21.4	37.2	0.58
Do.	Do.	Union sole.....	Union.....	8.3	2.7	2.5	13.2	14.8	28.0	6.4	6.1	27.5	33.4	0.82
Do.	Do.	Texas oak sole.....	Oak.....	8.3	1.7	1.5	13.7	13.1	26.8	4.0	5.3	28.5	34.6	0.82
Do.	Do.	Hemlock sole.....	Hemlock.	6.3	1.8	0.4	7.5	19.2	26.7	4.6	10.0	29.5	36.8	0.80
Do.	Do.	Texas scoured oak.....	Oak.....	7.3	0.7	2.0	14.8	7.1	21.9	0.4	2.3	28.0	40.5	0.69
Do.	Do.	Drum tanned.....	.....	7.6	0.9	0.7	13.4	2.9	16.3	1.2	0.0	26.1	49.0	0.53
Boston, Mass.....	Do.	Do.	.....	7.9	0.9	1.0	10.2	3.2	13.4	0.4	0.2	27.5	49.9	0.55
Do.	Do.	No. 1 sole, No. 2 bend.....	Union.....	8.8	1.9	3.2	14.4	16.1	30.5	4.4	9.2	23.8	33.4	0.71
Unknown.....	Do.	Scoured oak sole, No. 1 bend.	Oak.....	4.4	0.3	4.7	15.6	4.6	20.2	.....	1.1	33.0	37.4	0.88
Alexandria, Va....	Do.	Do.	Do.	3.6	0.2	3.3	14.9	5.1	20.0	.....	1.8	32.5	40.3	0.81
Do.	Do.	Scoured oak, extract tanned (in wheel after vat).....	Do.	3.8	0.3	3.5	14.2	5.0	19.2	.....	1.5	33.3	39.9	0.83
Do.	Do.	Vat-tanned belting, No. 1 butt	.....	4.9	0.2	5.3	11.5	5.5	17.0	.....	1.3	34.5	38.0	0.91
Do.	Do.	No. 2 side.....	Hemlock.	5.8	0.9	3.3	14.8	12.1	26.9	1.4	6.2	28.0	35.7	0.78
Do.	Do.	Oak.....	Union.....	5.9	1.2	4.5	14.2	9.7	23.9	2.4	2.7	30.8	34.6	0.89
Washington, D. C.	Do.	Scoured oak.....	Oak.....	6.3	1.0	5.5	13.6	10.8	24.4	3.0	2.5	27.7	35.8	0.77
Do.	Do.	Do.	Do.	7.0	0.6	3.7	13.2	6.8	20.0	.....	1.5	32.4	36.6	0.89
Do.	Do.	Do.	Do.	6.3	0.5	4.4	13.5	7.7	21.2	.....	2.0	28.0	39.8	0.70
Do.	Do.	Do.	Do.	5.5	1.0	1.9	12.6	17.9	30.5	2.1	7.2	26.8	35.0	0.77
Do.	Do.	Hard-rolled scoured oak.....	Do.	8.0	1.9	2.9	15.4	15.0	30.4	6.1	5.5	25.9	32.5	0.80
Do.	Do.	Do.	Do.	8.2	1.4	2.3	14.9	12.9	27.8	4.4	4.4	27.5	33.9	0.81
Do.	Do.	Scoured oak.....	Do.	6.9	1.5	2.5	10.1	12.5	22.6	1.0	6.1	27.7	40.0	0.69
Do.	Do.	Do.	Do.	7.7	1.5	3.1	9.3	10.7	20.0	0.5	5.1	26.4	42.5	0.62
Do.	Do.	Do.	Do.	8.9	2.4	1.2	12.5	14.9	27.4	2.8	4.0	30.0	32.2	0.93
Do.	Do.	Do.	Do.	8.2	1.4	1.5	13.4	11.6	25.0	4.1	2.4	29.5	35.5	0.83
Do.	Do.	Texas scoured oak.....	Do.	8.0	0.5	4.1	15.3	6.5	21.8	0.6	0.6	25.1	40.7	0.62
Do.	Do.	Do.	Do.	7.7	0.4	3.6	15.3	2.4	17.7	0.4	0.8	29.1	41.6	0.70
Do.	Do.	Scoured.....	Do.	7.6	1.0	4.4	9.4	10.9	20.3	3.2	2.8	26.7	40.7	0.66
Do.	Do.	Do.	Do.	8.9	0.9	3.6	11.6	8.5	20.1	2.3	2.1	23.3	43.8	0.53
Do.	Do.	Scoured oak sole.....	Do.	8.1	0.5	1.9	14.7	6.7	21.4	1.0	0.5	30.9	37.4	0.82
Do.	Do.	Do.	Do.	7.7	0.4	1.5	10.9	7.6	18.5	1.2	1.2	31.1	40.9	0.76



## ANALYSIS OF AMERICAN LEATHERS.—(Continued.)

Place sample was obtained	Time sample was obtained	Description of sample	Tannage claimed	Mois- ture, per cent.	Ash, per cent.	Petroleum ether extract, per cent.	Water-soluble material			Epsom salts, per cent.	Glu- cose, per cent.	Com- bined tannins, per cent.	Hide sub- stance, per cent.	Ratio of combined tannins to hide substance
							Tan- nins, per cent.	Non- tannins, per cent.	Total soluble, per cent.					
Baltimore, Md....	1912	Scoured oak.....	Do.	7.2	1.4	1.6	14.8	19.5	34.3	4.9	9.6	23.6	33.0	0.72
Do.	Do.	Do.	Do.	7.4	1.0	4.1	13.1	14.8	27.9	2.1	6.0	25.3	35.0	0.72
Do.	Do.	Texas scoured oak.....	Do.	8.2	0.6	3.4	11.9	7.5	19.4	0.3	1.6	32.3	36.4	0.88
Do.	Do.	Do.	Do.	8.9	0.4	2.0	13.6	5.9	19.5	.....	1.4	30.0	39.3	0.76
Do.	Do.	Scoured oak.....	Do.	8.8	1.5	1.0	13.6	18.7	32.3	4.5	3.5	25.2	32.4	0.78
Do.	Do.	Hemlock sole.....	Hemlock.	8.3	2.5	1.3	9.3	22.1	31.4	5.7	12.4	25.7	33.0	0.78
Do.	Do.	Do.	Do.	7.6	1.6	1.6	9.7	18.1	27.8	6.4	6.4	24.2	38.5	0.63
Do.	Do.	Union sole.....	Union...	8.7	1.5	2.5	14.6	13.4	28.0	4.1	5.5	27.4	33.1	0.83
Do.	Do.	Do.	Do.	7.4	2.0	3.7	13.5	11.0	24.5	3.8	5.4	28.5	35.6	0.80
Do.	Do.	Hemlock sole.....	Hemlock.	8.4	1.2	1.2	12.0	17.5	29.5	2.8	10.5	28.9	31.7	0.91
Do.	Do.	Do.	Do.	7.7	0.9	1.1	14.1	14.9	29.0	2.0	8.2	27.3	34.6	0.78
Do.	Do.	Scoured oak.....	Oak.....	8.2	0.3	1.3	13.7	6.1	19.8	.....	1.5	33.1	37.3	0.89
Do.	Do.	Do.	Do.	8.2	0.4	1.1	14.0	5.9	19.9	.....	1.2	31.3	39.2	0.80
Do.	Do.	Do.	Do.	12.3	0.5	0.9	10.9	7.1	18.0	.....	1.2	28.9	39.6	0.73
Do.	Do.	Do.	Do.	7.9	0.5	0.7	10.5	7.3	17.8	.....	1.5	32.4	40.9	0.79
Do.	Do.	Do.	Do.	8.4	1.2	1.1	13.2	14.5	27.7	1.9	5.9	27.0	35.5	0.76
Do.	Do.	Do.	Do.	8.6	0.9	2.3	12.0	12.6	24.6	2.5	5.6	27.0	37.2	0.73
Do.	Do.	Vat (no extract) scoured oak.	Do.	7.5	0.3	2.9	11.5	6.1	17.6	.....	1.8	29.5	42.2	0.69
Do.	Do.	Do.	Do.	7.6	0.3	2.6	12.9	4.7	17.6	.....	0.5	29.0	42.9	0.68
Alexandria, Va....	.....	Vat, chestnut oak extract, scoured oak.....	Do.	7.9	0.3	1.9	12.6	4.6	17.2	.....	0.4	34.2	38.5	0.89
Do.	Do.	Vat, chestnut oak extract, and quebracho.....	Do.	7.3	0.4	2.4	14.4	4.7	19.1	0.3	0.5	34.4	36.5	0.94
Do.	Do.	Do.	Do.	7.9	0.4	3.7	12.4	5.5	17.9	.....	0.4	33.3	36.9	0.90
Do.	Do.	Do.	Do.	8.2	0.2	1.5	14.4	6.3	20.7	.....	0.6	34.4	34.9	0.99
Do.	Do.	Do.	Do.	8.4	0.2	1.8	13.8	5.8	19.6	.....	0.5	34.8	35.1	0.99
Do.	Do.	Do.	Do.	5.8	0.7	3.6	17.3	9.8	27.1	.....	2.7	25.4	37.8	0.67
No. 1, Texas oak.....	1909	Do.	Do.	5.1	2.4	5.6	14.7	18.9	33.6	7.5	6.5	25.1	30.3	0.83
No. 2, union.....	Do.	No. 2, union.....	Union...	4.1	1.9	5.6	12.9	13.1	26.0	3.5	.....	27.1	36.9	0.73
No. 3, extract tanned, oak....	Do.	No. 3, extract tanned, oak....	Oak.....	4.1	1.3	4.1	14.5	12.7	27.2	3.1	3.6	26.8	37.5	0.71
No. 4, oak.....	Do.	No. 4, oak.....	Do.	4.2	1.6	2.5	16.2	10.2	26.4	3.9	3.4	28.3	38.3	0.74
No. 5, extract tanned, union..	Do.	No. 5, extract tanned, union..	Union...	3.4	1.0	4.0	14.2	11.4	25.6	2.9	4.3	29.3	37.4	0.78
No. 6, extract tanned.....	Do.	No. 6, extract tanned.....	Do.	3.6	0.9	1.8	11.7	12.9	24.6	2.1	.....	27.1	42.6	0.64
No. 7, weighted, hemlock.....	Do.	No. 7, weighted, hemlock.....	Hemlock.	4.7	1.2	1.9	11.6	17.4	28.7	2.1	5.9	29.7	34.7	0.86
No. 8, hemlock.....	Do.	No. 8, hemlock.....	Do.	4.2	1.1	2.0	14.2	11.3	25.5	2.7	3.7	28.7	39.3	0.73
No. 9, extract, union.....	Do.	No. 9, extract, union.....	Union...	4.2	1.1	2.0	14.2	11.3	25.5	2.7	3.7	28.7	39.3	0.73
No. 10, adulterated, South American dry hide.....	Do.	No. 10, adulterated, South American dry hide.....	Do.	4.7	2.7	2.9	15.5	21.2	36.7	3.8	2.8	25.8	29.6	0.87
No. 11, belly, oak.....	Do.	No. 11, belly, oak.....	Oak.....	5.4	0.5	3.8	11.4	13.0	24.4	.....	3.7	25.7	40.4	0.64
No. 12, extract, hemlock.....	Do.	No. 12, extract, hemlock.....	Hemlock.	5.6	0.4	1.4	15.8	7.6	23.4	.....	.....	26.2	43.1	0.60
No. 13, so-called oak.....	Do.	No. 13, so-called oak.....	Oak.....	6.3	1.5	3.5	9.2	12.2	24.4	4.7	3.6	27.3	38.2	0.71

Place sample was obtained	Time sample was obtained	Description of sample	Tannage claimed	Mois- ture, per cent.	Ash, per cent.	Petroleum ether extract, per cent.	Water-soluble material			Epsom salts, per cent.	Glu- cose, per cent. <sup>2</sup>	Com- bined tannins, per cent.	Hide sub- stance, per cent.	Ratio of combined tannins to hide substance
							Tan- nins, per cent.	Non- tannins, per cent.	Total soluble, per cent.					
Do.	1909	No. 14, oak.	Do.	4.3	0.7	3.4	6.1	10.6	16.7	...	5.2	29.1	46.2	0.63
Do.	Do.	No. 15, oak back.	Do.	4.8	0.8	4.3	13.7	10.3	24.0	...	5.6	26.7	39.9	0.67
Do.	Do.	No. 16, weighted, hemlock.	Hemlock.	5.7	1.9	2.3	14.9	20.2	35.1	3.4	10.7	24.4	32.2	0.76
Do.	Do.	No. 17, hemlock.	Do.	4.9	0.9	2.2	14.3	8.6	22.9	1.3	3.1	27.6	42.1	0.66
Do.	Do.	No. 18, South American dry hide, weighted.	Do.	4.3	1.0	2.9	13.7	17.3	31.0	4.3	5.6	30.0	31.5	0.95
Do.	Do.	No. 19, best.	Chrome <sup>1</sup> .	4.0	6.7	32.1	0.2	2.5	2.7	...	1.4	...	47.0	...
Do.	Do.	No. 20, best.	Chrome <sup>1</sup> .	2.9	6.0	34.6	0.2	2.9	3.1	...	1.4	...	54.9	...
Portsmouth, Ohio.	Do.	No. 1.	Union.	5.9	1.5	3.1	13.4	14.5	27.9	4.9	5.5	26.4	36.4	0.73
Do.	Do.	No. 2, oak.	Oak.	5.7	0.6	2.1	10.4	13.5	23.9	...	8.6	25.6	42.4	0.60
Do.	Do.	No. 3.	Union.	5.9	0.8	2.5	13.5	9.7	23.2	2.6	2.8	30.1	38.0	0.79
Do.	Do.	No. 4.	Oak.	5.2	0.3	3.5	11.7	7.8	19.5	...	1.2	30.7	40.8	0.75
Do.	Do.	No. 5.	Do.	5.8	0.3	1.4	12.0	7.6	19.6	...	1.5	31.0	41.9	0.74
Do.	Do.	No. 6.	Do.	5.6	0.4	0.9	8.9	19.6	28.5	0.2	8.0	24.6	40.1	0.60
Do.	Do.	No. 7.	Do.	6.4	0.3	1.3	12.2	7.0	19.2	...	0.9	29.4	43.4	0.68
Do.	Do.	No. 8.	Union.	4.8	0.9	2.5	12.1	9.8	21.9	0.2	3.8	28.0	42.5	0.66
Unknown.	Do.	Sole, lot No. 110, iron, not treated.	Do.	5.9	0.4	4.7	9.8	3.7	13.5	...	1.0	28.1	47.5	0.59
Do.	Do.	Sole, lot No. 210, iron, treated about 6 per cent.	Do.	6.2	2.3	2.0	10.0	13.5	23.5	0.2	9.2	26.7	41.3	0.65
Do.	Do.	No. 12.	Do.	5.6	0.8	1.2	12.0	12.1	24.6	...	0.8	27.3	41.0	0.67
Do.	Do.	Dark color.	Do.	5.3	0.2	4.3	12.2	5.8	18.0	...	1.4	36.4	35.7	1.01
Do.	Do.	Do.	Do.	5.4	0.3	2.9	10.7	5.9	16.6	...	1.0	40.3	34.5	1.16
Do.	Do.	Green yellow cast.	Oak.	4.9	0.3	2.5	14.1	4.3	18.4	...	0.8	31.2	42.7	0.73
Do.	Do.	Green yellow, redder than above.	Do.	5.6	0.3	1.4	14.5	4.4	18.9	...	0.9	31.8	42.0	0.75
Do.	Do.	Hemlock back.	Hemlock.	5.6	0.8	3.2	14.4	13.9	28.3	...	9.7	32.4	30.2	1.07
Washington, D. C.	Do.	Oak.	Do.	9.3	1.2	1.1	17.8	7.7	25.5	1.2	2.5	29.3	34.5	0.85
Alexandria, Va.	1910	Scoured oak sole.	Oak.	7.2	0.2	1.9	13.9	5.3	19.2	...	0.7	34.0	37.5	0.90
Washington, D. C.	1911	Flexible oak bend.	Do.	8.2	0.4	3.9	11.7	18.5	30.2	...	10.2	23.5	33.9	0.69
Do.	Do.	Oak sole.	Do.	8.9	0.2	4.0	12.9	5.3	18.2	...	0.7	20.9	41.8	0.64
Do.	1912	Do.	Union.	6.3	0.7	2.6	13.0	8.5	21.5	1.9	2.3	27.7	41.6	0.66
Portsmouth, Ohio.	Do.	Do.	Do.	5.9	1.0	1.1	11.2	10.1	21.3	3.8	4.2	29.2	42.2	0.69
Do.	Do.	Do.	Do.	6.8	1.5	2.9	12.5	11.8	24.3	4.6	4.6	27.8	37.9	0.73
Do.	Do.	Do.	Hemlock.	5.6	1.9	1.6	13.3	14.4	27.4	2.5	6.9	28.4	36.7	0.77
Do.	Do.	Do.	Oak.	5.9	0.7	2.5	14.8	7.7	22.5	1.5	1.7	28.7	40.1	0.71
Average.	...	...	...	6.6	1.1	3.4	12.8	10.5	23.3	2.7	3.8	28.5	38.2	0.75
Average in weighed samples.	...	...	...	...	...	...	...	...	...	...	...	...	...	...

<sup>1</sup> Sample No. 9713: 5.02 per cent. chromium trioxide in original sample.  
<sup>2</sup> Sample No. 9714: 1.32 per cent. chromium trioxide in original sample; 0.30 per cent. chromium trioxide in water soluble.  
<sup>3</sup> Procter allows anything over 2 % of glucose as adulteration.

manner. To determine the chromium and aluminium, 5 grm. of the leather are fused with 4 grm. sodium carbonate for half an hour. The chromium and aluminium are then present as chromate and aluminate and are estimated in the usual manner. It has been pointed out by J. Thuau that the separation of chromium from aluminium should always be effected owing to the increased use of chromium as a fore-tannage in the case of alum-tanned leather. Sometimes a light alum tannage also follows an all-chrome tannage.

Iron is determined in the usual manner if present.

#### ERRATUM IN VOL. V.

Page 105, line 6 for "Jeit" read "Zeit".

# ANALYSIS OF COLOURING MATERIALS.

By W. P. DREAPER, F. I. C.

## CHEMICAL EXAMINATION OF DYED FIBRES.

It is claimed by Holden<sup>1</sup> that direct and developed blacks on cotton may be distinguished from sulphide or aniline blacks by the following simple preliminary test:

The sample of dyed cloth is singed in a Bunsen flame. The part affected by the heat will change its colour. The substantive, developed or coupled class of blacks give a permanent light brown colouration at the singed portion while the sulphide and aniline black dyed cotton gives a faint black-brown colouration. It is claimed that the difference is easily distinguished and divides the blacks into two groups.

In the estimation of small quantities of dyestuffs more especially in food-stuffs W. E. Matthewson<sup>2</sup> oxidises with bromine water a few c.c. of the dye solution, the bromine being added gradually until the colour of the dye solution is destroyed. Hydrazine sulphate is then added to take up the excess of bromine and finally an excess of sodium carbonate. In a similar test a few drops of  $\beta$ -naphthol solution are added just before the sodium salt. Various colours result which have been recorded in the article referred to; in special cases the test might be of some value in textile work as a confirmation of other tests.

### Physical Examination of Dyed Fibres.

**Fastness of Colours.**—Owing to the unsatisfactory character of the methods of determining the "fastness" of colours against light and other reagents the Society of German Chemists appointed in 1911 a committee to deal with this question. As a result of this decision the committee recommended in 1911, that for the classification of dyestuffs in order of fastness five standards or grades should be adopted, 1 representing the least and 5 the greatest fastness. For each grade in each kind of fastness a typical dyestuff was to be given<sup>1</sup>.

Only the fastness of dyes on the fibre is dealt with, not that of the dyes themselves.

A sub-committee was appointed to prosecute further research, and the

<sup>1</sup> *J. Soc. Dyers and Col.*, 1913, 29, 36

<sup>2</sup> *Chem. News*, 1913, 265.

<sup>3</sup> *Chem. Zeit.*, 1914, 154.

results of the investigation were made known at a meeting of the section for dyeing and textile chemistry in May, 1912, when it was decided to increase the numbers of grades in the fastness to light section from five to eight.

In the selection of the typical dyestuff when a particular colour chosen was manufactured by several firms each product was submitted to the fastness tests.

A report of the committee was presented in Breslau in September, 1913, when it was resolved to publish the results of the investigation so far as it had then progressed.

1. **Fastness to Light.**—Parallel tests were made both open and under glass.

COTTON	WOOL
I.—5.5 % Chicago Blue 6B, 1 bath.	I.—3.15 % Indigotine I.
II.—1.0 % Methylene Blue BG.	II.—3.00 % Patent Blue A.
III.—1.0 % Indoine Blue R.	III.—3.25 % Amaranth.
IV.—20.0 % Kryogen Violet 3R, 1 bath.	IV.—4.4 % Azo Acid Red B.
V.—2.5 % Benzo Light Red 8BL, 1 bath.	V.—5.00 % Acid Violet 4RN.
VI.—9.0 % Hydron Blue G paste, 1 bath.	VI.—2.5 % Diamine Fast Red F., chromed.
VII.—8.0 % Kryogen Black, 1 bath.	VII.—4.00 % Anthraquinone Green GXN.
VIII.—25.0 % Indanthrene Blue GC paste, 1 bath.	VIII.—Indigo Pure.

2a. **Fastness to Washing and Boiling of Dyed Cotton in Contact with White Cotton.**—(A) The sample is plaited with white cotton and treated for  $\frac{1}{2}$  hour at 40° C. in fifty times its amount of a 0.2 % solution of Marseilles soap. The plait is then wrung out by hand, soaked in the soap solution and again wrung out, this being repeated ten times. The cotton is then washed and dried.

(B) This is a more severe test. The solution contains 0.5 % of soap and 0.3 % of sodium carbonate, and the cotton is kept in the boiling solution for  $\frac{1}{2}$  hour, then cooled to 40° C. and wrung as in A.

GRADE	TYPICAL DYESTUFF
I.—Treated as in A. Colour a little lighter, white cotton dyed.	I.—3 % Benzopurpurin 4B, dyed for 1 hour at the boil with 20 grm. of Glauber's salt cryst. to the litre. An equal quantity of Glauber's salt is then added and the dyeing continued for 15 minutes longer.
II.—Treated as in A. Colour unchanged, white cotton not at all or only slightly dyed.	II.—5 % Primuline dyed as in I., then diasotised and coupled with $\beta$ -naphthol. Soaped with 0.2 % soap for 5 minutes at 35° C.
III.—Treated as in B. Colour a little lighter, white cotton only slightly tinted.	III.—2.5 % Indoine Blue BB on yarn previously mordanted with 6 % tannin and 3 % antimony salt. Dyed with addition of 5 % acetic acid $\frac{1}{4}$ hour cold, $\frac{1}{2}$ hour heating up to boiling, and $\frac{1}{4}$ hour at the boil.
IV.—Treated as in B. Colour unchanged, white cotton only faintly dyed.	IV.—12 % Immedial Indone R conc., dyed at the boil for 1 hour with $1\frac{1}{2}$ times its weight of sodium sulphide cryst. in a bath containing 3 grm. soda and 20 grm. sodium chloride to the litre. After 1 hour an equal amount of sodium chloride is added and the dyeing continued for $\frac{1}{4}$ hour longer.
V.—Treated as in B. Colour unchanged, white cotton not at all or only slightly tinged.	Or Indigo dyed from a hydrosulphite bath. V.—Alizarin Red.

2b. **Fastness to Washing of Dyed Wool in Contact with White Wool or Cotton.**—(A) The sample, plaited with wool or cotton, is heated for  $\frac{1}{4}$  hour at 40° C. with 50 times its amount of a solution containing 10 grm. of Marseilles soap and 0.5 grm. sodium carbonate in a litre, then wrung out five times with the hands, washed and dried.

(B) The same treatment at 80° C. for  $\frac{1}{4}$  hour.

**Fastness in Contact with Wool.****GRADE**

I.—Treated as in A. Colour much changed, pronounced bleeding to the white.

III.—Treated as in A. Little or no change in colour; no bleeding to the white.

V.—Treated as in B. Little or no change in colour; no bleeding to the white.

**TYPICAL DYESTUFF**

I.—2% Orange II dyed with 10% Glauber's salt cryst. and 10% sodium bisulphate for 1 hour at the boil.

III.—2% Patent Blue A dyed with 10% Glauber's salt cryst. and 3% acetic acid. Dyeing commenced at 40° C. and heated within 20 minutes to boiling, and kept at the boil for 1 hour. 2% H<sub>2</sub>SO<sub>4</sub> added after 1/2 hour's boiling.

V.—7% Palatine Chrome Black 6B dyed with 10% Glauber's salt cryst. and 3% acetic acid. Commenced at 60° C., raised to boiling in 15 minutes. After 1/2 hour's boiling 2% H<sub>2</sub>SO<sub>4</sub> added, cooled to 70° C., 2.5% of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> added, and kept just at the boil for 40 minutes.

**Fastness in Contact with Cotton.**

I.—Treated as in A. Pronounced bleeding into the white.

III.—Treated as in A. No bleeding into the white.

V.—Treated as in B. No bleeding into the white.

I.—2% Chrysophenin G dyed with 10% Glauber's salt cryst. Entered at 40° C., raised to boiling in 20 minutes and kept at the boil for 1 hour. 2% acetic acid added after 3/4 hour boiling.

III.—2% Patent Blue A dyed as before.

V.—7% Palatine Chrome Black 6B dyed as before.

(3a) **Fastness to Water of Dyed Cotton.**—The sample is plaited with boiled-off white cotton, washed Zephyr wool, and white silk, taking two parts of the dyed sample to one part of the white material. It is allowed to remain for 1 hour in cold distilled water (about 20° C.) and then dried at the ordinary temperature.

**GRADE**

I.—With a single treatment the colour is somewhat lighter and the white material coloured.

III.—With a single treatment colour unaffected and white material not changed.

V.—With three successive treatments (each with fresh water) colour unaffected and white material not changed.

**TYPICAL DYESTUFF**

I.—2% Chrysophenin G dyed as in 2a, I.

III.—2% Chloramine Yellow dyed like I.

V.—8% Immedial Carbon B dyed as in 2a, IV.

(3b) **Fastness to Water of Dyed Wool.**—Treatment as in 3a, but 12 hours' duration.

**GRADE**

I.—With a single treatment colour changed and white material coloured.

III.—With a single treatment colour unchanged, no bleeding into the white.

V.—With three successive treatments (each time with fresh water) colour unchanged, bleeding, none or very slight.

**TYPICAL DYESTUFF**

I.—2% Azo Yellow dyed at the boil for 1 hour with 10% Glauber's salt and 10% sodium bisulphate.

III.—2% Patent Blue dyed as in 2b.

V.—7% Palatine Chrome Black 6B dyed as in 2b.

(4) **Fastness to Rubbing** (for all dyeings).—White unfinished cotton cloth is rubbed vigorously with the sample ten times backwards and forwards over a length of 10 cm.

(5a) **Fastness to Ironing of Dyed Cotton.**—The sample is covered with a doubled sheet of thin white unfinished cotton cloth which is moistened with water (100% water), and is ironed with an iron of such a temperature that with the same pressure it will just begin to scorch a piece of white flannel. The ironing is continued until the moist covering is quite dry.

**GRADE**

I.—Colour much altered, and bleeds into the white cloth.

III.—Colour a little changed, but does not bleed.

V.—Colour not changed and does not bleed.

**TYPICAL DYESTUFF**

I.—1.5% Methylene Blue B dyed for 1 1/4 hours with 20 times the cotton weight of distilled water and 2% acetic acid. The cotton is first mordanted with 6% of tannin and 3% antimony salt.

III.—1% Benzopurpurin 4B dyed as in 2a.

V.—1% Chloramine Yellow C dyed as in 2a, I.

(5b) **Fastness to Ironing of Dyed Wool.**—The sample is pressed for 10 seconds with a hot iron of such a temperature that with the same pressure it does not scorch a piece of white flannel.

GRADE	TYPICAL DYESTUFF
I.—Colour much changed, and does not return to the original shade on cooling.	I.—Magenta S dyed with 10% Glauber's salt cryst. and 10% sodium bisulphate for 1 hour at the boil.
III.—Colour apparently changed, but quickly returns to the original shade on cooling.	III.—2% Amaranth dyed with 10% Glauber's salt cryst. and 10% sodium bisulphate at 60° C., heated to the boil in 20 minutes and kept for 1 hour at the boil.
V.—No change in the colour.	V.—2% Tartrazine dyed with 20% Glauber's salt cryst. and 10% sodium bisulphate at the boil.

(6) **Fastness to Sulphur of Dyed Cotton and Wool.**—The sample, plaited with an equal quantity of wool is soaped for 5 minutes at the ordinary temperature in a  $\frac{1}{2}\%$  solution of Marseilles soap. It is then wrung out and introduced into an atmosphere charged with sulphur dioxide, where it remains for 12 hours.

#### Sulphur Fastness of Dyed Cotton.

GRADE	TYPICAL DYESTUFF
I.—Colour changed, white wool coloured.	I.—1% Diamond Magenta dyed like Methylene Blue (5a) on a tannin-antimony mordant.
III.—Colour slightly changed, white wool not coloured.	III.—1% Columbia Black FF extra dyed as in 2a, I.
V.—Colour and white wool unchanged.	V.—1% Diamine Black B dyed as in 2b, I.

#### Sulphur Fastness of Dyed Wool.

I.—Fairly pronounced change in the colour, but scarcely any bleeding.	I.—2% Diamine Scarlet B dyed as in 2b, I.
III.—Slight change in the colour, scarcely any bleeding.	III.—2% Milling Red G dyed with 10% Glauber's salt cryst., 2% acetic acid, commencing at 30° C., heating to boiling in 20 to 30 minutes, and dyeing for 1 hour at the boil. After $\frac{3}{4}$ hour boiling 3% acetic acid is added.
V.—No change in the colour, and little or no bleeding.	V.—2% Palatine Black A dyed with 10% Glauber's salt cryst., 10% sodium bisulphate. Beginning at 60° C., heating to boiling in 20 minutes, and dyeing for 1 hour at the boil.

(7a) **Fastness of Dyed Cotton to Perspiration.**—The sample is plaited with the same quantity of white boiled-off cotton, and is heated for 10 minutes at 80° C. in a solution of ammonium acetate containing 5 c.c. of neutral ammonium acetate (30%) in a litre of distilled water. It is then dried without washing.

GRADE.	TYPICAL DYESTUFF
I.—Colour lighter, white cotton strongly coloured.	I.—1% Chrysophenin G dyed as in 2a, I.
III.—Colour unchanged, white cotton coloured.	III.—1% Diamine Black BH directly dyed as above.
V.—Colour and white cotton remain unchanged.	V.—20% Indanthrene Blue RS paste.

(7b) **Fastness of Dyed Wool to Perspiration.**—(A) Treatment with sodium chloride solution. The sample is spotted with a 10% NaCl solution, dried at the ordinary temperature, and then well brushed.

GRADE	TYPICAL DYESTUFF.
I.—Marked change in the colour.	I.—2% Amaranth dyed with 10% Glauber's salt cryst., 10% sodium bisulphate, beginning at 60° C., raising in 20 minutes to boiling, and keeping at the boil for 1 hour.
III.—The colour is fairly strongly changed.	III.—2% Wool Green S dyed with 10% Glauber's salt and 10% sodium bisulphate for 1 hour at the boil.
V.—No change in the colour.	V.—2% Brilliant Crocein 3B dyed with 10% Glauber's salt and 10% sodium bisulphate, beginning at 60° C., raising in 20 minutes to the boil, and dyeing at the boil for 1 hour.



(B) Treatment with ammonium acetate. As with the cotton, but the sample is plaited with both wool and cotton.

GRADE.	TYPICAL DYESTUFF
I.—Colour not or only slightly changed, white wool and cotton are tinted.	I.—2 % Azo Yellow dyed as in 3b.
III.—Colour not changed, white cotton unchanged, wool slightly dyed.	III.—2 % Amaranth dyed as in 5b.
V.—Colour not changed, neither wool nor cotton dyed.	V.—7 % Palatine Black 6B dyed as in 2b.

(8) Fastness to Alkali of Dyed Cotton and Wool (Dust Fastness).—10 grm. of quicklime and 10 grm. of 24% ammonia are made to a cream with 1 litre of water. The dyed sample is spotted with this, dried without washing at the ordinary temperature, and then well brushed.

### Wool.

GRADE	TYPICAL DYESTUFF
I.—Much altered.	I.—2 % Water Blue dyed with 10 % sodium bisulphate, beginning at 60° C., heating to boiling in 20 minutes, and then boiling for about 3/4 hour.
III.—Fairly pronounced change in the colour.	III.—2 % Amaranth dyed as in 5b.
V.—No change in the colour.	V.—7 % Palatine Chrome Black 6B dyed as in 2b.

### Cotton.

GRADE	TYPICAL DYESTUFF
I.—Much altered.	I.—1.5 % Malachite Green conc. dyed with a tannin-antimony mordant as in 5a, I.
III.—Fairly pronounced change.	III.—1 % Direct Deep Black E extra dyed as in 2a, I.
V.—No change.	V.—8 % Diamine Black BH dyed as in 2a II.

(9a) Fastness of Dyed Cotton to the Acid Boil.—The sample is plaited with wool and cotton and boiled for 1 hour with forty times the amount of a solution of cream of tartar containing 10% of the latter on the weight of the cotton.

GRADE	TYPICAL DYESTUFF
I.—Colour only a little lighter, white wool dyed.	I.—2 % Chloramine Yellow C dyed as in 2a I.
III.—Colour not or only slightly changed, white wool only slightly dyed.	III.—3 % Primuline developed with $\beta$ -naphthol as in 2a, IV.
V.—Colour unchanged, wool and cotton not dyed.	V.—8 % Immedial Carbon B dyed as in 2a, IV.

(9b) Fastness of Dyed Wool to the Acid Boil.—The sample is plaited with washed Zephyr wool and treated in seventy times the quantity of a 0.25% solution of bisulphate of soda for 1½ hours at 90–92° C.

GRADE.	TYPICAL DYESTUFF
I.—Colour slightly changed, white wool dyed.	I.—2 % Chrome Yellow D dyed with 10 % Glauber's salt cryst. and 3 % acetic acid, beginning at 60° C., and heating to boiling in 15 minutes. The bath is kept at the boil for 1/2 hour, then 2 % sulphuric acid is added, and, after cooling to 70° C., 1.25 % of $K_2Cr_2O_7$ . Finally, it is boiled gently for 30 minutes.
III.—Colour unchanged, white wool only slightly dyed.	III.—2 % Diamine Scarlet B dyed as in 2b, I.
V.—Colour unchanged, white wool not at all or only very slightly tinted.	V.—6 % Alizarin Black WX extra paste dyed with 10 % Glauber's salt and 5 % acetic acid. First at 60° C., heated to boiling in 20 minutes; after 1/2 hour boiling 5 % acetic acid added. After a further 20 minutes' boiling the bath is cooled to 70° C., 2 % $K_2Cr_2O_7$ added, and the bath gently boiled for 40 minutes.

(10) Fastness to Acid of Dyed Cotton.—The sample is spotted with mineral acids (10% sulphuric acid) and with organic acids (30% acetic),

and the change in shade compared with that of a place spotted with pure water.

GRADE	TYPICAL DYESTUFF
I.—With mineral acids strongly, with organic acids only slightly changed.	I.—3 % Diamine Scarlet B.
III.—With mineral acids strongly, with organic acids not changed.	III.—0.5 % Chrysophenin G.
V.—With mineral acids or organic acids no change.	V.—20 % Indanthren Blue RS paste.

(11) **Fastness of Dyed Cotton to Scouring.**—The dyed cotton is treated with the same weight of unbleached undyed cotton. Two methods of testing are adopted: (A) Scouring in an open boiler with 7.5%  $\text{Na}_2\text{CO}_3$ , 0.5% Marseilles soap, and 1% Ludigol calculated on the weight of the material; proportion of material to liquor 1:5; duration of operation, 6 hours. (B) The same process without the Ludigol.

GRADE	TYPICAL DYESTUFF
I.—By treatment A completely destroyed.	I.—Congo Red.
II.—By treatment A almost completely destroyed.	II.—Methylene Blue B.
III.—By treatment A very much changed.	III.—Indigo.
IV.—Resists treatment A.	IV.—Helindone Orange R.
V.—Resists treatment B.	V.—Turkey Red.

(12) **Fastness of Dyed Cotton to Chlorine.**—The sample is plaited with the same quantity of boiled-off white cotton and treated for 1 hour at about 15° C. in a freshly prepared bath of chloride of lime containing 1 gram. of active chlorine to the litre, or of sodium hypochlorite containing the same percentage of active chlorine and not more than 0.3 gram. of soda to the litre.

GRADE	TYPICAL DYESTUFF
I.—With sodium hypochlorite, colour lighter, bleeding to the white. With calcium hypochlorite, much lighter, bleeding into white.	I.—1 % Methylene Blue B dyed with a tannin-antimony mordant as in 5a.
II.—With sodium hypochlorite, colour changed but does not bleed. With calcium hypochlorite, much changed but does not bleed.	II.—6 % Indanthrene Olive G powder, dyed with 20 times the cotton weight of distilled water with addition of 5 times the dyestuff weight of NaOH (76 Tw.) and 2½ times of hydrosulphite for ½ hour at 60° C.
III.—With sodium hypochlorite, colour a little lighter, no bleeding. With calcium hypochlorite, much lighter, no bleeding.	III.—Indigo as in 2a, I.
IV.—With sodium hypochlorite, colour not changed, no bleeding. With calcium hypochlorite, somewhat lighter, no bleeding.	IV.—10 % Hydron Blue G paste dyed with half the weight of NaOH (76 Tw.) and half the weight of hydrosulphite. Otherwise as Indanthrene Olive (II.).
V.—Colour unchanged with both reagents, no bleeding.	V.—Ordinary Turkey Red dyeing.

(13) **Fastness to Mercerising of Dyed Cotton.**—Yarn dyed with the colouring matter to be tested is sewn into bleached unfinished cotton cloth and treated for 5 minutes in cold sodium hydroxide of 52° Tw.

I.—Colour slightly changed, some bleeding into the white.	I.—4 % Primuline developed with $\beta$ -naphthol as in 2a.
III.—Colour unchanged, very slight tinging of white.	III.—1 % Chloramine Yellow C dyed as in 2a, I.
V.—Colour unchanged, no bleeding.	V.—8 % Immedial Carbon B dyed as in 2a, IV.

(14) **Fastness to Bleaching of Dyed Wool.**—White threads of wool, cotton, and silk are sewn into the dyed sample of woollen cloth, which is then treated with hydrogen peroxide. The bleaching bath is prepared with

100 parts of distilled water and 20 parts of hydrogen peroxide (10–12% vol.), and this solution is made just alkaline with ammonia. The bath must remain weakly alkaline (to Congo Red paper) throughout the operation. The sample is brought into the bath at an initial temperature of 45–50° C., and is allowed to remain for 12 hours in the gradually cooling liquid.

GRADE	TYPICAL DYESTUFF
I.—Colour only slightly changed, but bleeds slightly into the wool, silk, and cotton.	I.—2% Azo Yellow dyed as 3b.
II.—Colour is lighter and bleeds slightly into the wool, silk, and cotton.	II.—2% Patent Blue A dyed as in 2b.
III.—Colour is lighter but does not bleed.	III.—2% Fast Yellow S dyed as for Azo Yellow in 3b.
IV.—Colour not or only slightly changed, bleeds a little into the silk and cotton but not to the wool.	IV.—2% Chrysophenin G dyed as in 2b.
V.—Colour not or only slightly changed. Does not bleed, or only very slightly.	V.—2% Sulphocyanin GR extra dyed with 2% Glauber's salt cryst. and 5% ammonium acetate, commencing at 40° C., heating within ½ hour to 80–90° C., and keeping at this temperature for ¾ hour.

(15) **Fastness to Milling of Dyed Wool.**—(A) Neutral milling The sample is plaited with an equal quantity of white wool and cotton and then treated at 30° C. in forty times the quantity of a milling liquor containing 20 gm. of Marseilles soap to the litre. The sample is well worked with the hand, this being continued at intervals for 2 hours.

(B) The sample is treated at 40° C. in a solution containing 20 gm. Marseilles soap and 5 gm. sodium carbonate per litre.

### With White Wool.

GRADE	TYPICAL DYESTUFF
I.—Treated as in A. Pronounced change in the colour and bleeding.	I.—2% Azo Yellow dyed as in 3b.
II.—Treated as in A. Slight change in the colour, slight bleeding.	II.—2% Ponceau RR dyed as for Orange II. in 2b.
III.—Treated as in A. No change or only slight in the colour, no bleeding.	III.—6% Sulphocyanin Black 2B dyed as in 14 V.
IV.—Treated as in B. No change or only slight in the colour, slight bleeding.	IV.—2% Chrome Yellow D dyed as in 9b.
V.—Treated as in B. Colour not or only slightly changed, no bleeding.	V.—7% Anthracene Chrome Black P extra dyed as in 2b, V.

### With White Cotton.

GRADE	TYPICAL DYESTUFF
I.—Much bleeding into the white.	I.—2% Diamine Scarlet B dyed as in 2b.
II.—Slight bleeding into the white.	II.—2% Ponceau RR dyed as for Orange II. in 2b.
III.—No bleeding.	III.—6% Sulphocyanin Black 2B dyed as in 14 V.
IV.—Slight bleeding.	IV.—5% Diamond Black F chromed with 1.5% K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> after dyeing as in 2b.
V.—No bleeding.	V.—7% Diamond Black PV dyed as in 2b.

(16) **Fastness to Carbonisation (Wool).**—The sample is soaked in sulphuric acid of 7.4° Tw., pressed so as to contain 100% of the solution, then dried at 80° C. for ¼ hour. The sample is then washed with 200 times its amount of distilled water for ¼ hour, and then for ¼ hour in a 0.2% solution of sodium carbonate. Finally, it is washed with water until neutral.

GRADE	TYPICAL DYESTUFF
I.—Strong change in the colour.	I.—2% Alizarin Red W powder dyed on wool previously mordanted by boiling for 1½ hours with 3% $K_2Cr_2O_7$ and 2½% sodium bisulphate. The dyeing is done in a fresh bath with 2% acetic acid added. Commenced at 30° C., heated to boiling in ½ hour, and kept at the boil for 1½ hours.
III.—Slight change in the colour.	III.—2% Orange IV dyed with 10% Glauber's salt cryst., and 10% sodium bisulphate for 1 hour at the boil.
V.—Colour unchanged or only slightly changed.	V.—2% Palatine Scarlet A dyed with 10% Glauber's salt cryst., 10% sodium bisulphate, at a commencing temperature of 60° C., heating in 20 minutes to, and keeping for 1 hour at the boil.

(17) **Fastness of Dyed Wool to Potting.**—A. The sample is plaited with the same quantity of white wool and cotton and treated for 2 hours in sixty times the amount of hot distilled water at 90° C.

(B) Like A with distilled water containing 1 gram. of Marseilles soap to the litre.

GRADE	TYPICAL DYESTUFF
I.—Treated as in A. The colour is changed, white wool or cotton strongly coloured.	I.—2% Patent Blue A dyed as in 2b.
III.—Treated as in A. The colour is not or is only slightly changed, slight colouring of the white wool or cotton.	III.—5% Diamond Black F dyed as in 2b, V., but chromed afterwards with 1½% $K_2Cr_2O_7$ .
V.—Treated as in B. Colour not changed at all or only slightly, no bleeding.	V.—7% Alizarin Black WX extra dyed as in 2b, V.

(18) **Fastness of Dyed Wool to Steam Pressing.**—A. The sample is rolled on a steam cylinder and steamed for 5 minutes in the closed apparatus at 14 pounds pressure.

(B) The same for 10 minutes at 35 pounds pressure.

GRADE	TYPICAL DYESTUFF
I.—Treated as in A. Fairly strong change in the colour.	I.—2 per cent. Sulphocyanin GR extra dyed as in 14, V.
III.—Treated as in A. No change in the colour.	III.—2 per cent. Crocein AZ dyed like Brilliant Crocein 3B in 7b.
V.—Treated as in B. No change in the colour.	V.—9 per cent. Naphthol Black 6B dyed with 10% sodium bisulphate. Dyeing commenced at 40° C., brought to boiling in 30 minutes, and dyed at the boil for 1 hour.

(19) **Fastness of Dyed Wool to Seawater.**—The sample is plaited with the same quantity of white wool and allowed to stand for 24 hours in forty times the quantity of a cold solution of 30 gram. NaCl and 6 gram.  $CaCl_2$  in the litre, then dried without washing.

GRADE	TYPICAL DYESTUFF
I.—Colour only slightly changed, much bleeding to the white.	I.—2% Chrysoin dyed as in 3b, I.
III.—Colour not at all or only slightly changed, some bleeding to the white.	III.—2% Cyanol extra dyed as in 2b, III.
V.—Colour unchanged, no bleeding.	V.—6% Sulphocyanin Black dyed as in 14, V.

The above tests must be used with great care by the general analyst. They are purely empirical, as the dyestuffs used as standards are only of commercial purity.

# COLOURING MATTERS OF NATURAL ORIGIN.

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By W. M. GARDNER, M.Sc., F. I. C.

The natural dyestuffs are used in slowly diminishing quantity and a few only are now of commercial importance. With the exception of indigo, no natural dyestuff has received much attention from the analytical point of view in recent years, but considerable work has recently been published on the estimation of this product

## Indigo.

An exhaustive paper dealing with the estimation of indigo on dyed wool materials has been published by Green, Gardner, Lloyd and Frank.<sup>1</sup> It comprises: I. a critical examination of all previously published methods; II. a description of new methods for the quantitative estimation of indigo by weight; and, III. methods for the determination of the proportion of the total depth of shade which is due to indigo when other dyestuffs have been used in conjunction.

**I. Examination of Known Methods of Analysis.**—With the object of submitting these methods to critical investigation it was decided in the first place to employ, instead of indigo-dyed materials, pieces of undyed woollen cloth, or woollen cloth dyed with colouring matters usually employed for topping or bottoming, in which were wrapped weighed quantities of pure indigotin. Such cloth was then submitted to the extraction methods recommended by the various authors, and the recovered indigo either weighed as such or submitted to sulphonation with concentrated sulphuric acid at 70° C. and estimated by titration with *N*/50 potassium permanganate.

**Experiments with Rawson's Hydrosulphite Method.**—The indigo is separated from the cloth by reduction with an alkaline solution of sodium hydrosulphite, precipitated from the solution by aeration, filtered off, and weighed or estimated volumetrically, after sulphonation, by titration with permanganate.

The indigo separated by this method is apparently very pure, but the process is tedious, a large volume of liquid having to be filtered. The method gives moderately good results with lightly dyed materials, but somewhat variable results with heavily dyed, thick, felted cloths.

<sup>1</sup> *J. Soc. Dyers and Colourists*, 1913, 29, 227–241.

The method has been compared by Binz and Rung<sup>1</sup> with the acetic acid extraction method (which follows), and they find that the latter is less troublesome and more rapid, whilst the results are somewhat higher.

**Experiments with Brylinski's Method.**—Brylinski<sup>2</sup> extracts the material in a Soxhlet apparatus with glacial acetic acid, afterwards diluting the solution with water, filtering off the precipitated indigo on a weighed filter, washing with alcohol and ether, and finally drying and weighing. The method was improved by Binz and Rung<sup>3</sup> who dilute the acetic acid extract with a smaller quantity of water and mix in a separating funnel with ether. The indigo becomes suspended in the ether, leaving the aqueous acetic acid layer almost clear. The indigo can then be readily separated from the ether by filtration through a hardened filter paper, washed with alcohol and ether, dried, and weighed. Binz and Rung have found that a portion of the indigo is decomposed during the long boiling necessary for the extraction, and this they attribute to the reducing action of the wool. The authors have however proved that the loss is due to the decomposition by heat of indigo which has crystallised out upon the sides of the boiling flask.

The use of paper, even parchmentised paper, for filtration was found objectionable, (1) on account of its liability to vary in weight, and (2) because the precipitated indigo cannot be subjected to sufficiently rigorous treatment with reagents to remove impurities.

**Experiments with Möhlau and Zimmerman's Method.**—Möhlau and Zimmerman<sup>4</sup> are credited with having simplified and shortened the method of estimating indigo on the fibre by means of acetic-sulphuric acid. In this method, 10 grm. of the material, which is cut as fine as possible, are heated in a flask or beaker, on a rapidly boiling water-bath, with 100 c.c. of acetic-sulphuric acid (100 c.c. glacial acetic acid and 4 c.c. concentrated sulphuric acid) for about half an hour, shaking occasionally. The hot solution is filtered through a Gooch crucible, using hardened filter paper, the residue being repeatedly heated on the water-bath with acetic-sulphuric acid and filtered until the filtrate is no longer blue. The extract is warmed to 50° to redissolve the indigo, and is then diluted to twice its volume with boiling water. After cooling, the indigo is filtered off on a weighed, hardened filter paper, well washed with hot water until the filtrate is no longer acid, then with a little alcohol, and finally with 100 c.c. of ether, dried at 110°, and weighed. From the percentage of indigo obtained there is deducted for cotton materials 0.22%, this being the amount of modified cellulose supposed to be present with the indigo. With woollens no correction is considered necessary, since it is assumed that the dissolved wool remains in solution on dilution.

<sup>1</sup> *Zeit. angew. Chem.*, 1898, 904.

<sup>2</sup> *Rev. Gen. Mat. Col.*, 1898, 54; 1899, 5; *J. Soc. Dyers and Colourists*, 1898, 75.

<sup>3</sup> *Zeit. angew. Chem.*, 1898, 904.

<sup>4</sup> *Zeit. Farb. Text. Chem.*, 1903, 189.

This method gives very variable results, and the difficulty of manipulation is greatly increased when certain topping or bottoming colours are present, *e.g.*, logwood, myrabolans, etc.

**Experiments with Other Proposed Extraction Methods.**—The extraction of indigo from the fibre by solvents has generally been carried out in a Soxhlet apparatus, and the following substances, in addition to acetic acid, have been proposed for the purpose: Phenol, aniline,<sup>1</sup> naphthalene,<sup>2</sup> and nitrobenzene.<sup>3</sup> In using these solvents for extracting weighed quantities of pure indigo from wool, low results are obtained. The largest percentage error was obtained with nitrobenzene; naphthalene came next, then aniline, and lastly phenol. From this it appears that the chemical properties of the respective solvents, as well as their boiling points, play an important rôle in the quantitative extraction of the indigo. None of the above solvents is as suitable as acetic acid.

The extraction of indigo from dyed materials by solvents, followed by sulphonation and estimation of the indigo by examining the colour of the solution tintometrically (in place of titration with permanganate) was also found unsatisfactory, concordant tintometric or colourimetric readings being very difficult to obtain.

**II. New Methods of Analysis.**—In the hope of finding a solvent capable of effecting a more rapid extraction of the indigo from the dyed material, whilst at the same time leaving unaffected any topping or bottoming colour which might be present, experiments have been made by the authors with numerous organic liquids. The following are the results obtained:

(a) Pyridine (pure or commercial) is a valuable solvent for the extraction of indigo. It removes the indigo quantitatively and more rapidly than does acetic acid, leaving the wool in better condition and with less loss of wool substance. In a number of cases in which the topping or bottoming colours are removed by acetic acid, they are but little affected by pyridine.

(b) Piperidine extracts indigo quantitatively, and has practically the same properties as pyridine, but is much more expensive.

(c) Anisole also extracts indigo quantitatively, but lacks sufficient solvent power for practical use.

(d) Epichlorhydrin dissolves indigo slowly, giving a clear blue solution. The extraction though slow is quantitative.

(e) Dichlorhydrin dissolves indigo, giving a green solution. The indigo may be completely removed from dyed fabrics, but cannot be estimated by means of this solvent, as some decomposition takes place.

(f) Formic acid, 90%, extracts indigo more readily than does glacial acetic acid, but attacks the wool to a greater extent.

(g) Indigo is removed from the fibre, though not very readily, by

<sup>1</sup> Koenig, *Zeit. f. ang. Chem.*, 1889, 10.

<sup>2</sup> Schneider, *Zeit. Anal. Chem.*, 1895; *J. Soc. Dyers and Colourists*, 1895, 194.

<sup>3</sup> Gerland, *J. Soc. Chem. Ind.*, 1896, 17; 1897, 100.



chloroacetic ether; more slowly by amyl alcohol, amyl acetate, cumene, and perchlorethylene.

(h) Benzaldehyde removes indigo from the fibre very rapidly; at the same time combining with the indigo to form a soluble yellow compound. Many topping or bottoming colours, which are stripped from the fibre both by acetic acid and by pyridine, are but little affected if the indigo is removed by benzaldehyde. It is therefore useless for the estimation of indigo, but is of value for the rapid qualitative testing of a dyed cloth.

(i) Cresol has long been known as a good solvent for indigo, but it attacks the wool too seriously to be used at its boiling point. It has, however, proved a most satisfactory agent when diluted with about 25% of a neutral hydrocarbon, such as "solvent naphtha" or "turpentine substitute," so as to give a liquid which will extract in an ordinary Soxhlet extractor at a temperature of from 100° to 110°C. By this means the indigo can be removed completely in nearly all cases without disturbing the concomitant dyestuffs, which can then be examined or quantitatively determined.

Of the solvents experimented with, only glacial acetic acid, pyridine, benzaldehyde, and the cresol mixture appear to be capable of practical employment. The special use of each of these will be referred to later.

**Improvements in Extraction Apparatus.**—In the extraction method, as hitherto employed, the operation is unduly prolonged and frequently incomplete by reason of the fact that in the ordinary Soxhlet extractor the solvent is much below its boiling point when it comes into contact with the fibre.

It has been found that a great advantage is gained in extraction by solvents if means are taken to effect the extraction at the actual boiling point of the solvent instead of at the lower temperature usually obtained in the Soxhlet apparatus. By using the solvent at its boiling point, the time for extraction is greatly decreased. Thus, when using glacial acetic acid or pyridine as solvents, the thickest materials can be completely extracted in 4 hours at most, whilst ordinary materials do not require more than 1½ to 2 hours. Extraction at the boiling point is effected by employing one of the forms of extractor which have been devised by L. L. Lloyd for this purpose (see Fig. 1, forms A, B, and C, on page 431).

If the form A is used the weighed cloth is placed loosely in the siphon tube, which is surrounded by an outer tube F. through which the vapour passes. If the cloth is packed too tightly, indigo separates in a crystalline form on the inner surface of the tube, and is only slowly redissolved. The solvent is condensed by an air or water condenser E., and flows into the siphon tube, from which it is intermittently siphoned over into the distilling flask D. The extraction is continued until a blue extract is no longer obtained. To detect whether the whole of the indigo has been extracted, the Bunsen flame is regulated so that the liquid in the extraction tube just fails to siphon over, and the solvent is kept in contact with the material for about 10 minutes.

If the extraction is complete, the liquid will not be coloured. In the case of material which easily separates short fibres, it is preferable to pack it loosely in an inner tube drawn out at the end and provided with glass points to support it in the siphon tube. Some crushed quartz is placed in the latter to act as filter, and to prevent short fibres from closing up the fine opening in the tube.

In the form of apparatus B, the cloth is placed loosely in the extraction

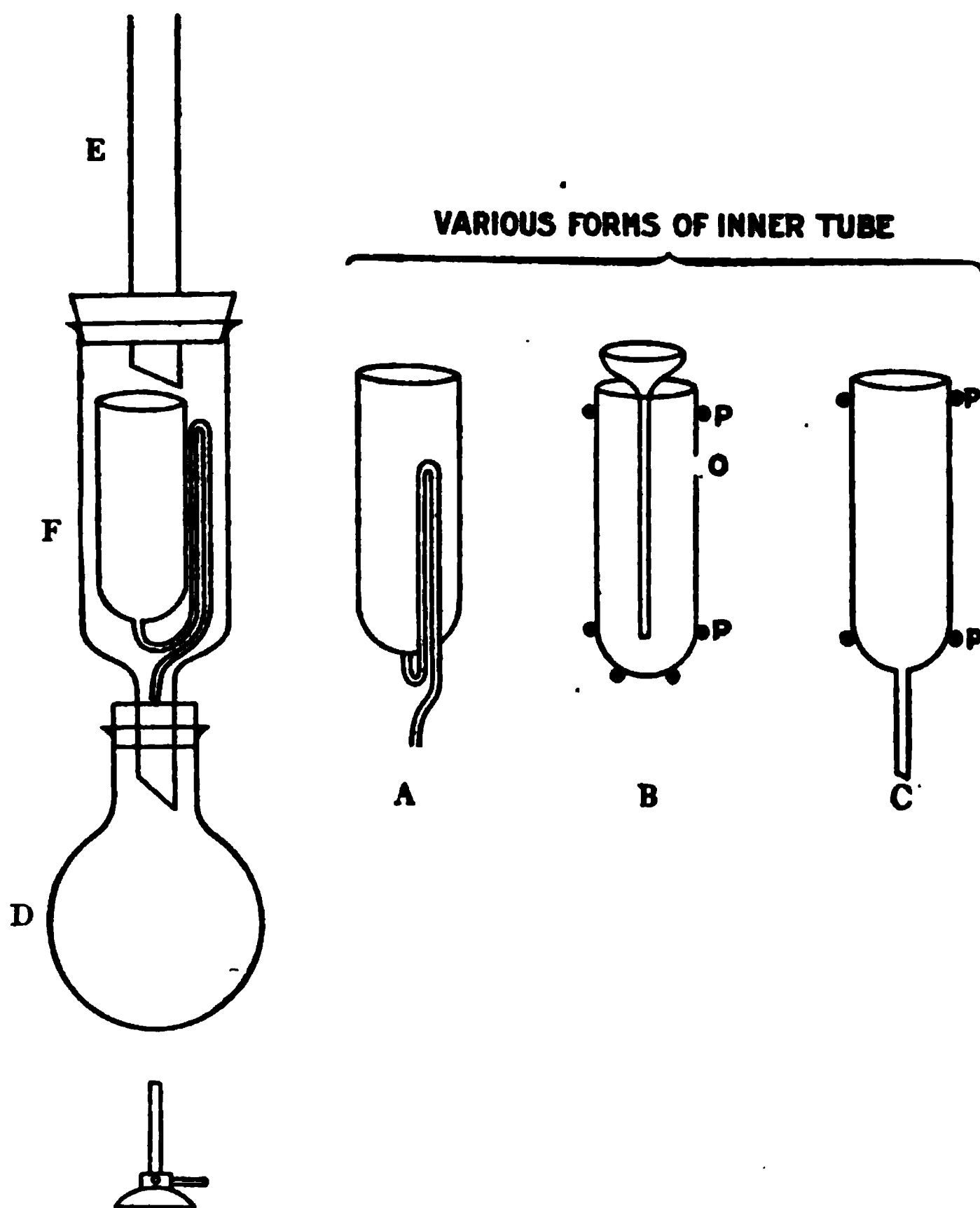


FIG. 15.

tube and the condensed solvent directed to the bottom by means of a long, drawn-out funnel tube, the solvent then overflowing from the side opening (o) in the extraction tube.

The simpler form of apparatus C is found to give good results for most cloths, and is easy to make. The extraction tube is drawn out at the end, some glass points (p) being fused on to the outer surface so as to furnish a

passage round it for the vapour of the solvent. A little white wool, cotton wool, or crushed quartz is placed in the tube, as a filtering and regulating medium, and also to retain short fibres. The orifice and packing should be so adjusted as to prevent the condensed solvent from running through too quickly thus insuring the accumulation of a head of liquid above the cloth. This may be partially regulated by the flame and also by the packing of the cloth and filtering medium.

Lloyd finds the form of apparatus A the most satisfactory for most kinds of fabrics, but recommends the tube B for loosely woven and open cloths.

The form C is found by Frank to be suitable for most materials and is employed by Lloyd for loose wool, yarn, and other materials easily separated into fibres, the threads, if necessary, being held in position by covering with a small filter plate.

In the extraction of indigo from heavily-dyed, thick, felted cloth, it is recommended to cut the material into small pieces or strips and to commence the extraction in the apparatus C, afterwards placing the tube containing the partially extracted material in the siphon tube A.

The weight of the cloth to be taken for gravimetric estimations varies from 3 to 15 grm., viz., sufficient to give from 0.03 to 0.10 grm. of indigo.

**Further Experiments upon Acetic Acid Extraction.**—The extraction of the indigo is accompanied by a certain loss of weight in the wool, and the extracted wool substance is not soluble in water, but is precipitated with the indigo, which accounts for the incorrect results obtained when such precipitated indigo is sulphonated and estimated by titration.

The wool substance is completely removed from the extracted indigo by means of boiling dilute sulphuric acid (20% by volume) without affecting the indigo, and this may be done by washing the filtered indigo upon a Gooch crucible, or glass filtering tube, using glass wool as the filtering medium. The wool substance is more quickly removed from the extracted indigo by washing with sulphuric acid as above, followed by boiling dilute ammonia (1:3), or boiling 10% sodium hydroxide, the preliminary treatment with sulphuric acid preventing the alkali from forming a colloidal solution of the indigo, which will pass through the filter. If gravimetric estimation is employed and the indigo is collected and weighed repeatedly in the same filtering tube, the indigo remaining in the tube serves as a filtering medium, and in this case the washing with boiling sulphuric acid can be omitted, the precipitate being washed directly with boiling ammonia or sodium hydroxide.

The following perfected method for analysis by acetic acid extraction has been finally adopted (Lloyd): The indigo is extracted at the boiling point in any of the forms of apparatus already described, using 3 to 15 grm. of material according to the percentage of indigo present. From 50 to 70 c.c

of glacial acetic acid are employed, and with the extractor A or B an additional quantity sufficient to fill the extraction tube and cause it to siphon or overflow. At the end of the extraction the tube is left filled with the solvent. If the material is easily extracted, the boiling-flask may be heated over wire gauze, but when the time of extraction exceeds 2 hours the flask should be heated in an oil-bath. Under these conditions the amount of decomposition is not sufficient to affect the accuracy of the process for technical purposes.

The extract is allowed to stand until cold and is then filtered through a weighed glass tube containing quartz or glass wool, or upon a Gooch crucible. The indigo is washed twice with 10 c.c. of cold glacial acetic acid, then with 20 c.c. of boiling dilute acetic acid (30% by volume), and afterwards with water. To remove wool substance and colouring matters, the indigo is then well washed with boiling dilute sulphuric acid (20% by volume), the acid is removed by washing with water, and the indigo is then well washed with boiling ammonia (1:3) or with boiling 10% sodium hydroxide until the filtrate is no longer coloured. The alkali is now removed by washing with boiling water, then with a small quantity of acetic acid, again with boiling water, and finally with about 20 c.c. of alcohol. The filter is now dried at 110° and weighed. The washing with 20% sulphuric acid is only necessary when a new filter is used.

A slight modification of the above described method of procedure is employed by Frank, who works in the following manner: The extraction is effected in the tube C, employing 70 to 100 c.c. of glacial acetic acid. The extract is allowed to cool, diluted with 100 c.c. of 50% alcohol, heated nearly to boiling and filtered hot through a Gooch crucible, containing coarse asbestos as filtering medium. These crucibles are readily prepared by keeping some asbestos soaking in 50% acetic acid and using as required. The collected indigo is washed with water, hot 2% sodium hydroxide, boiling dilute hydrochloric acid (3:100), and finally with alcohol and ether. It is then dried for a short time in the water oven, put into a small beaker, and sulphonated at 70°–75° with 15–20 c.c. of pure conc. sulphuric acid for three-quarters of an hour. After cooling, it is poured into water, made up to 500 c.c., and titrated with *N*/10 permanganate, using 100 c.c. at a time, diluted with 200 c.c. of water. The indigo content is obtained from the factor 1 c.c. *N*/10 permanganate = 0.00146 grm. of indigo.

**Experiments on the Estimation of Indigo by Extraction with Pyridine.**—The powerful solvent action of pyridine upon indigo renders this liquid particularly suitable for extracting indigo from the fibre, and superior in many respects to acetic acid.

The extraction may be carried out in any of the forms of extracting apparatus already described. When form C is used the material is made into a loose roll, or is wrapped in fine wire gauze, and put into the extraction tube; but felted, heavily milled, or tightly woven cloth is cut into thin strips. A little cotton wool is placed at the bottom of the tube to collect small fibres

and to prevent the too rapid percolation of the condensed solvent, thus keeping the tube full of liquid.

To ascertain whether the extractions with pyridine were quantitative, and also to determine the most suitable working conditions, experiments were carried out by wrapping weighed quantities of indigo in wool, union, and cotton fabrics, then subjecting these to extraction, and weighing the indigo recovered. It was found that the wool was not attacked by pyridine, even upon long boiling, to as great an extent as occurs when acetic acid is used, but unless sufficient solvent is employed to keep the whole of the indigo in solution, heating of the boiling flask over a bare flame may cause a certain amount of decomposition of the indigo which crystallises on the sides of the flask. It was also observed that when a solution of indigo in pyridine is allowed to stand, a gradual disappearance of the colour occurs in the course of a few days, apparently through air oxidation, and it is therefore advisable to filter the extract without delay. If the extraction is effected in the siphon extracting tube, it is necessary to employ pyridine of fairly constant boiling point, but with the other forms of apparatus a good commercial pyridine may be used.

The wool substance is not dissolved to the same extent by pyridine as by acetic acid, and caustic soda completely removes the impurity from the precipitate.

That the wool is less attacked is also shown by the smaller loss of weight which it suffers, averaging 1.8% against 5.5 to 6% in extractions with acetic acid, after allowing in each case for the indigo present.

Indigo is far more soluble in cold pyridine than in cold glacial acetic acid, and the amount left in solution after cooling renders it necessary to precipitate the whole of the indigo by addition of a solvent miscible with pyridine in which indigo is insoluble.

When a pure indigo-dyed cloth was extracted with 100 c.c. of pyridine, filtered off after 1 hour's standing on ice, and the indigo present in the blue filtrate neglected, the percentage found was 1.23. On the other hand, 1.28% of indigo was obtained when the filtrate was concentrated and diluted with 50% alcohol.

Iron lakes of tannin materials are fairly easily decomposed by pyridine, and when the wool has been heavily loaded with iron, some difficulty may be encountered owing to precipitation in the boiling flask. The precipitated indigo may also require a more protracted washing with acid and alkali.

But although the direct extraction of such materials may yield slightly high results, the previous removal of the topping dyestuff and iron is not advisable and may even give rise to a small loss of indigo.

The use of pyridine has especial advantages in the analysis of thick, felted, heavily milled or hard spun twill materials, which are very troublesome and difficult to extract completely by means of acetic acid.

It also has the advantage of leaving the wool in a better condition than does acetic acid.

The following table (Lloyd) gives the limits of accuracy in the various methods of analysis which have been examined:

	Possible error. (Percentage upon total indigo)
I. Rawson's hydrosulphite method.....	0 to -13
II. Brylinski's method.....	+30.0 to +44.7
III. Acetic acid extraction followed by after-treatment with caustic soda.....	- 1.7 to - 2.8
IV. Möhlau and Zimmermann's method.....	- 3.8 to -11.0
V. Acetic acid extraction followed by washing with 20% sulphuric acid and caustic soda or ammonia	- 0.5 to + 3.1
VI. Preceding method when other dyestuffs are present	- 1.3 to + 3.1
VII. Pyridine extraction without after-treatment of precipitate.....	+ 8.7 to +30.0
VIII. Pyridine extraction followed by washing with 20% sulphuric acid and caustic soda or ammonia....	- 2.2 to - 4.0
IX. Preceding method when other dyestuffs are present	- 3.4 to + 1.5

The following method of procedure has been finally adopted for **analysis by pyridine**: The extraction tube (usually form C is preferred) is charged with from 3 to 15 gm. of material (viz., sufficient to give about 0.05 gm. of indigo), the hole at the bottom of the tube being covered with a little cotton wool. Cloth is made into a loose roll or is enclosed in thin wire gauze. 100 c.c. of commercial pyridine (b. p. 110°-127°) are put into the boiling flask, which is heated over wire gauze or upon an air-bath. Either a water condenser, or simply a long air condenser, is employed. The extraction is continued until the pyridine runs through quite colourless, which usually requires from 2 to 3 hours. The extract is then distilled down to about 20 or 30 c.c., the pyridine recovered being kept for future extractions. The extraction flask is then set aside to cool, when the greater part of the indigo separates in well-formed bronzy crystals. To complete the precipitation of the indigo, 150 c.c. of 50% alcohol are added, and after heating to boiling, the liquid is filtered either through an ordinary Gooch crucible prepared with filter paper or asbestos, or through a glass filtering tube containing glass wool.

Before weighing the filter for use, it is washed with exactly the same liquids as are to be used for washing the precipitated indigo and then dried at 110°. The filtration through a Gooch crucible is very rapid, taking less than 2 minutes. The precipitate is washed on the filter successively with hot 50% alcohol, hot 2% caustic soda, hot dilute hydrochloric acid (3:100), hot water, alcohol, and finally ether. The crucible is then dried at 110° and weighed. Lloyd prefers to wash with 20% sulphuric acid and then with hot 10% caustic soda or ammonia, then with 20 c.c. of glacial acetic acid, finally with water and with alcohol. The appearance of the indigo precipitate is a guide to its purity. It should form a bronzy crystalline powder, which, when analysed by the Bloxam-Perkin method,<sup>1</sup> tests 100%.

<sup>1</sup>See Vol. V, p. 394.



A dull appearance shows the presence of impurities. In order to shorten the operation it is advisable after about  $\frac{3}{4}$  of an hour's extraction to remove and repack the material in the tube, placing what was formerly inside in the outside position. Heavy materials should be cut into fine strips and also repacked after some time. If it is desired to estimate the indigo by titration instead of by direct weighing, the precipitate is collected on a Gooch crucible, the bottom of which is covered with a little asbestos. After washing with acid and alkali as above, and drying for a short time, the crucible is placed in a small beaker containing 15 to 20 c.c. of pure concentrated sulphuric acid, and the indigo is sulphonated by heating in an oven to  $70^{\circ}$ – $80^{\circ}$  for 45 minutes. The solution is then made up to 500 c.c. and titrated with  $N/50$  permanganate, using 100 c.c. at a time, diluted with 200 c.c. of water. The percentage of indigo is found from the factor 1 c.c.  $N/50$  permanganate = 0.00146 grm. indigo (Frank), or = 0.00147 grm. (Lloyd), obtained by sulphonating pure sublimed indigo and titrating in the same way. This factor is more exact than that employed by Rawson, viz., 0.00150.

In treating cloths which have been heavily topped with iron and tannin materials, Lloyd thinks it advisable to remove as far as possible these lakes, prior to the pyridine extraction, by alternate boiling with a solution containing 5% oxalic acid, and with dilute ammonia (5:100), until colour is no longer extracted. Frank, however, considers that this previous treatment of the dyed cloth is unnecessary, provided the extracted indigo is efficiently washed with acid and alkali as described above.

**Analysis of Commercial Indigo-dyed Materials by the Pyridine and Acetic Acid Methods.**—Both the acetic acid and pyridine methods are capable of giving accurate results under the conditions laid down.

In order to subject these methods of analysis to a rigid test, and at the same time to effect a comparison between them, analyses were carried out upon a large number of materials dyed under practical conditions, the results of which are given in the tables which follow. The first series represents a range of pure indigo shades, from a light blue to a very dark navy. The second series consists of a medium shade of indigo-dyed cloth which was afterwards topped with a variety of acid and mordant colouring matters. In the third series the wool was bottomed with various colouring matters and afterwards dyed in the indigo vat. The colouring matters selected as topping or bottoming colours were those most likely to be employed in practice. The fourth series consists of a variety of commercial indigo and navy blue cloths of different makes. The fifth series contains a number of official and Government cloths. In series six the same dyestuffs are employed both as bottoming and topping colours, in order to ascertain whether the total tintometric value of the mixed shade is thereby affected.

The analyses were made gravimetrically with pyridine and both gravimetrically and volumetrically with acetic acid.



SERIES I.

Reference number	Description	Percentage indigo found		
		Acetic acid or other solvent <sup>1</sup> by weight (Lloyd)	Acetic acid by titration with KMnO <sub>4</sub> (Frank)	Pyridine by weight (Frank)
		%	%	%
1	Pure indigo.....	0.42	0.54	0.44
2	Pure indigo.....	0.51	0.66	0.54
3	Pure indigo.....	0.71	0.75	0.64
4	Pure indigo.....	0.85	0.92	0.80
5	Pure indigo.....	1.14	1.08	1.05
6	Pure indigo.....	1.30	1.29	1.25
7	Pure indigo.....	1.46	1.44	1.33
8	Pure indigo.....	1.68	1.71	1.70
9	Pure indigo.....	2.13	2.20	2.27
10	Pure indigo.....	2.43	2.50	2.50
59	Pure indigo.....	2.23	2.10	2.10
60	Pure indigo.....	2.47	2.41	2.35
61	Pure indigo.....	2.72	2.95	2.71
62	Pure indigo.....	3.69	3.54	3.42
63	Pure indigo.....	4.57	4.43	4.42

SERIES II. (TOPPED BLUES.)

Reference number	Description	Percentage of indigo found		
		Acetic acid or other solvent <sup>1</sup> by weight (Lloyd)	Acetic acid by titration with KMnO <sub>4</sub> (Frank)	Pyridine by weight (Frank)
		%	%	%
13	Standard Indigo, bottomed with 2 % chrome alone....	1.68	1.79	1.73
	Standard Indigo, topped with:			
14	2 % bichromate and 2 % Sulphon Cyanine 5R extra..	1.69	1.72	1.72
15	2 % bichromate and 1½ % Brilliant Aliz. Blue R pdr..	1.71	1.74	1.67
16	1½ % Topping Violet RTN (B.A.S.F.).....	1.67	1.76	1.66
17	2 % Indocyanine 2R (Ber. Co.).....	1.68	....	1.72
18	1½ % Erio Fast Purple A (Geigy).....	1.69	1.77	1.69
19	2 % Fast Acid Violet R (M. L. & B.).....	1.71	1.75	1.72
20	1¼ % bichromate and 2 % Chrome Blue A (B.A.S.F.)..	1.64	1.73	1.70
21	1¼ % bichromate and 2 % Palatine Chrome Blue B..	1.59	1.78	1.77
22	2 % bichromate and 2 % Hematine crystals.....	1.70	1.68	1.70
23	1¼ % bichromate and 2 % Eriochrome Azurol B.....	1.65	1.72	1.68
24	1¼ % bichromate and 2 % Omega Chrome Cyanine B..	1.68	1.67	1.62
25	2 % bichromate and 1¼ % Alizarin Blue B.....	1.71	1.68	1.69
26	2 % bichromate and 8 % Alizarin Blue GW double...	1.67	....	1.65
27	2 % bichromate and 2 % Sulphon Dark Blue 2B.....	1.72	1.69	1.72
28	2 % bichromate and 2 % Wool Fast Blue BL (By)...	1.67	1.74	1.62
29	2 % bichromate and 2 % Sulphon Cyanine GR extra..	1.69	1.69	1.65
30	2 % bichromate and 1½ % Indochromine 2R conc....	1.73	1.69	1.69
31	2 % bichromate and 20 % Cudbear.....	1.70	1.65	1.65
39	2 % bichromate and 7 % Gallein paste.....	1.67	1.74	1.66
40	2 % bichromate and 7 % Gallocyanin paste.....	1.74	1.73	1.62
41	2 % bichromate and 5 % Alizarin Cyanin 3R double paste.	1.69	1.73	1.60
42	2 % bichromate and 2 % Lanacyl Violet B (Cass.)...	1.65	1.76	1.69
43	2 % bichromate and 2 % Soluble Blue (L. D. Co.)....	1.69	1.73	1.68
44	2 % bichromate and 2 % Acid Chrome Blue 2R (By)..	1.65	1.75	1.65
45	2 % bichromate and 2 % Eriochrome Blue BR (Gy)..	1.67	1.74	1.62
46	1 % Acid Violet 4BRS (Sandoz).....	1.70	1.76	1.72
47	1½ % Omega Light Violet R (Sandoz).....	1.72	1.75	1.72
50	Myrabolans and "nitrate of iron".....	1.71	1.73	1.66
55	3 % bichromate and 3¼ % Fustic.....	1.73	1.72	1.64
56	2 % Picric Acid.....	1.70	1.76	1.68
57	2 % bichromate and Logwood.....	1.72	1.70	1.62
58	Myrabolans and ferrous sulphate.....	1.72	1.65	1.63
83	Indigo extract.....	1.66	....	1.66
	Standard Indigo filled with:			
85	Starch.....	1.62	1.60	1.62
86	Magnesium chloride.....	1.61	....	1.62

<sup>1</sup> Some of these figures are the average of several obtained with acetic acid, pyridine, and piperidine

SERIES III. (BOTTOMED BLUES.)

Reference number	Description	Percentage of indigo found		
		Acetic acid or other solvent <sup>1</sup> by weight (Lloyd)	Acetic acid by titration with KMnO <sub>4</sub> (Frank)	Pyridine by weight (Frank)
32	Bottomed with: 1 % Azo Fuchsine G..... 2 % bichromate and 8 % Cudbear..... 2 % bichromate and 1 % Aliz. Red IWS (M) 2 % bichromate and 20 % Sanderswood..... 2 % bichromate and 30 % Camwood..... 2 % bichromate and 20 % Barwood..... 1 % bichromate and 1 % Omega Chrome Red B. All dyed together in same indigo vat.	%	%	%
33		2.20	2.37	2.14
34		2.16	2.02	1.97
35		2.09	2.07	1.94
36		2.13	2.00	1.98
37		2.23	2.05	2.02
38		2.14	2.05	1.96
		2.20	2.13	2.08

SERIES IV. (BLUES ON VARIOUS MATERIALS.)

Reference number	Description	Percentage of indigo found		
		Acetic acid or other solvent <sup>1</sup> by weight (Lloyd)	Acetic acid by titration (Frank)	Pyridine by weight (Frank)
64	Pure indigo on 2-ply worsted	%	%	%
65	Pure indigo on fine woollen	1.64	1.65	1.58
66	Pure indigo on fine merino....	1.98	1.97	1.89
67	Pure indigo on coarse worsted	2.30	2.40	2.28
68	Lighter shade of No. 64.....	1.61	1.78	1.54
69	Lighter shade of No. 65	0.51	0.49	0.48
70	Lighter shade of No. 66	0.70	0.54	0.55
71	Lighter shade of No. 67	0.84	0.73	0.75
84	Indigo on cotton warp material.....	0.69	0.54	0.54
51	A commercial indigo.....	1.72	....	1.63
52	Another commercial indigo.....	0.98	0.71	0.71
53	No. 1 Navy blue.....	1.03	0.70	0.65
54	"Pure" indigo on worsted cloth (red bottom).....	3.86	3.76	3.80
12	No. 2 navy blue on grey serge.....	3.44	....	3.41
		2.38	....	2.32

SERIES V. (OFFICIAL AND GOVERNMENT STANDARDS.)

Reference number	Description	Percentage of indigo found by extraction with pyridine (by weight)	
		(Lloyd) <sup>2</sup>	(Frank)
72	No. 1 customs.....	%	%
73	No. 2 custom worsted.....	2.52	2.35
74	No. 3 blue.....	2.59	2.54
75	(Old) Pantaloon cloth.....	4.18	4.18
76	Post-office pilot.....	3.35	3.23
77	4A blue.....	3.12	3.22
78	Box cloth.....	3.25	3.0
79	4B blue.....	4.20	4.23
80	(Old) Metropolitan Police blue.....	2.60	2.54
81	No. 2 artillery.....	2.90	2.82
82	Navy tartan.....	3.04	3.11
87	Metropolitan Police, blue greatcoat.....	3.03	2.91
		2.46	2.50

<sup>1</sup> Some of these figures are the average of several obtained with acetic acid, pyridine, and piperidine.  
<sup>2</sup> In some cases analyses were made with piperidine as well as with pyridine.

SERIES VI. (EFFECT OF TOPPING OR BOTTOMING ON TOTAL SHADE.)

Reference number	Description	Percentage of indigo found	
		Acetic acid or other solvent <sup>1</sup> by weight (Lloyd)	Pyridine by weight (Frank)
109	White cloth dyed with Indigo.....	% 1.36	% 1.34
110	Bottomed with ¾% bichromate and 1% Eriochrome Red BR...	1.54	1.56
111	1% Eriochrome Red BR without chrome.....	1.53	1.54
112	2% bichromate and 1% Alizarin Red IWS.....	1.32	1.34
113	Previously chromed wool (2% chrome) dyed with Indigo.	1.37	1.47
114	Indigo, No. 109, topped with 1% Eriochrome Red BR and ¾% bichromate.....	1.35	1.36
115	1% Eriochrome Red BR without bichromate.....	1.33	1.36
116	1% Alizarin Red IWS and 2% bichromate.....	1.26	1.41
117	Indigo, No. 113, topped with 1% Eriochrome Red BR and ¾% bichromate.....	1.37	1.48
118	1% Eriochrome Red BR without bichromate.....	1.36	1.48
119	1% Alizarin Red IWS and 2% bichromate.....	1.24	1.46

III. Determination of Percentage Colour Effect Due to Indigo.—It is obvious that the simple statement of the percentage of indigo upon a cloth, as found by analysis, does not afford to anybody but an expert an idea of the quality of the dye. What is required by manufacturers, merchants, and the public is a means of knowing what proportion of the total depth of colour is due to the indigo present. The solution of this problem is a difficult one, as besides the difficulty of finding an instrument capable of accurately measuring depth of colour on fabrics, the dyestuffs accompanying the indigo are not necessarily blue, but are frequently violet or red. A solution has been attempted by employing the Lovibond tintometer as the colour-measuring instrument. Since the relative proportions of red, yellow, and blue will vary in different shades, the measure of depth must be taken as the total number of colour units obtained by adding together the units of red, yellow, and blue, given by the glasses required to match the pattern. By applying this instrument to the series of shades of pure indigo, dyed on white wool, of which the analyses are given in the table Series I, it has been found that the depths of shade thus expressed lie upon a regular curve (see Fig. 2, p. 440). There is thus a definite relation between the percentage of indigo on the material by weight and the tintometric reading. The tintometer readings from which this curve is constructed are given in the following table. These readings were obtained in a north light between 10 a. m. and 12 a. m. on February 18, 1914, a bright morning with light blue sky and white clouds:

<sup>1</sup> Some of these figures are the average of several experiments with different solvents.

Reference number	Percentage of indigo present (by analysis). (Mean result)	Tintometer measurements			
		Red	Yellow	Blue	Total units
1	0.45	4.0	2.6	10.9	17.5
2	0.53	4.9	2.9	11.4	19.2
3	0.70	6.1	3.4	12.1	21.6
4	0.83	7.1	3.5	12.7	23.3
5	1.05	8.4	3.5	12.96	24.86
6	1.23	9.0	4.0	13.0	26.0
7	1.40	9.6	4.3	13.1	27.0
8	1.70	10.8	4.7	13.5	29.2
9	2.20	11.7	5.0	13.6	31.3
10	2.30	12.2	6.6	13.7	32.5
61	2.71	12.5	8.3	13.0	33.8
62	3.38	13.2	9.4	14.0	36.6
63	4.45	13.7	9.8	14.5	38.0

Percentage of Indigo.

Total Tintometer Units.

FIG. 16.

By employment of such a curve it is possible (assuming its accuracy) to determine from the tintometric readings of a given cloth, the percentage of indigo it contains if dyed with indigo only; or when dyed with other colours in addition, the percentage of indigo which would be required to give a shade of corresponding depth if indigo alone was used. Furthermore, in this case it is possible when the actual percentage of pure indigo on the cloth, as determined by analysis, is known, to express the colour effect due to the latter (obtained from the curve) as a percentage of the total colour, measured in terms of the amount of indigo which would be required to give the total depth of shade of the pattern if indigo alone was used. This ratio, termed the "percentage colour effect due to indigo," is given by the expression:

$$x = \frac{A \times 100}{C}$$

in which A = the percentage of indigo found by analysis and C = percentage of indigo given by the curve corresponding to the total tintometer units of the

**pattern.** This value cannot be obtained from the direct ratio between the tintometer colour units corresponding to the indigo present and the total shade units, since the depth of shade is not directly proportional to the amount of dyestuffs present, but increases at a constantly diminishing rate as the shade becomes darker. It has been ascertained by examination of a large number of patterns dyed with pure indigo (Series IV) that the same percentage of indigo gives substantially the same tintometric reading for all classes of material composed of wool independently of the quality and weave. The variation observed is certainly less than 1 in 20, the tintometric reading being slightly higher for thick materials than for thin. It has also been established that in mixed shades the tintometric reading is the same whether the additional dyestuff has been employed as a bottoming or as a topping colour (see Series VI).

Experiments made with this method have shown that for blues of light and medium depth (up to, say, 2.5% of indigo) results of sufficient exactitude for commercial purposes can be obtained, but that for heavy shades which approach black the tintometer is incapable of measuring colour depth with sufficient accuracy, since with dark shades a relatively large increase in the percentage of indigo produces only a small increase in the tintometric reading.

Standard conditions for reading the tintometer cannot be laid down, as somewhat different readings are obtained for the same pattern on different days on account of variations in daylight. The readings of different observers may also vary on account of differences of light, eyesight, and instrument. It is therefore recommended that in applying this method the curve given above should only be used as an approximation and should be corrected at the time of use by taking tintometer readings of a series of four or five pure indigo shades kept as standards, in which the percentages of indigo have been accurately determined by analysis. Having also obtained by analysis the percentage of indigo in the material under examination, the value for the "percentage colour effect due to indigo" can then be deduced from the corrected curve. For example, a sample of cloth dyed with indigo and topped with other dyestuffs is found to contain 1.5% of indigo by analysis, and gives a total reading of 32.5 colour units on Lovibond's tintometer. From the curve it is seen that a shade dyed with pure indigo to give a reading of 32.5 colour units has to contain 2.4% of indigo. Therefore, the "percentage colour effect due to indigo" on the pattern is:

$$\frac{1.5 \times 100}{2.4} = 62.5$$

All the analyses and tintometer measurements are made upon cloth containing its "condition moisture," usually about 14%.

For the investigation of heavy shades, with which the above method of deducing the "percentage colour effect due to indigo" is unreliable, another

method is available which, so far as the experiments go, appears to be capable of giving satisfactory results with all depths of shade. This consists in entirely removing the indigo from the pattern by extraction with a suitable solvent and measuring the depth of the residual colour (dyestuff used for topping or bottoming) in total colour units by the Lovibond tintometer. The indigo equivalent of this residual colour (= B) is then found from the curve, and knowing the actual percentage of indigo present on the cloth, as determined by gravimetric analysis (= A), the “percentage colour effect due to indigo” is given by the equation:

$$x = \frac{100 A}{A + B}$$

In order to test this method of procedure and to compare it with the previous one, five navy blue serges were tested by the tintometer, together with the bottoming dyes (mainly Alizarin Reds) upon which they were dyed, and also the same serge dyed simultaneously on a white bottom in the same vat, and therefore containing approximately the same quantity of indigo. In each case the total number of tintometer units found were translated by means of the curve into percentage indigo equivalents, the following numbers being obtained:.

Number of sample	Indigo equivalents from curve (percentages)		
	Blue dyed on white serge	Red bottom (= B)	Compound shade (= C)
1	2.41	0.38	2.84
2	1.55	0.48	2.10
3	1.35	0.50	1.85
4	1.46	0.78	2.30
5	1.96	1.25	3.25

The actual indigo present on the patterns was found by analysis to be as follows:

Number of sample	Percentage indigo present		
	Indigo on white serge	Indigo Compound shade	Average (= A)
1	2.39	2.29	2.34
2	1.52	1.52	1.52
3	1.28	1.33	1.31
4	1.44	1.41	1.42
5	1.85	1.88	1.86

Calculating for these five patterns the “percentage colour effect due to indigo,” firstly from the tintometer readings alone, and secondly by making use of the two equations:

I.  $x = \frac{100 A}{C}$     II.  $x = \frac{100 A}{A + B}$

the following results are obtained:

Number of sample	Percentage colour effect due to indigo		
	From tintometer values alone	By method I	By method II
1	82.2	84.8	86.0
2	72.4	73.8	76.0
3	70.8	72.9	72.4
4	61.7	63.5	64.5
5	57.2	60.3	59.8

The results by the different methods are therefore in good accord.

To be in a position to make use of the second method it is necessary to be able to strip the indigo completely from a compound shade and to leave the topping or bottoming colour practically unaltered. A small *change* of shade of the latter does not matter, provided the *depth* is not affected. In a large number of cases the stripping may be satisfactorily done by employing either boiling glacial acetic acid or boiling pyridine as the stripping agent, for whereas many dyes are removed from wool by one or the other of these solvents, comparatively few of them are stripped by both, those which are dissolved by the one being usually not affected by the other. In using these solvents care should be taken that they are anhydrous, as a small percentage of water increases their solvent action on dyestuffs other than indigo. The acetic acid should therefore be frozen and the separated crystals remelted, whilst the pyridine should be carefully dried over solid sodium hydroxide. For the same reason, the pattern to be extracted should be previously dried in a steam oven.

As there are a few colouring matters which are removed from the wool by both acetic acid and by pyridine, some other solvent is occasionally necessary. Benzaldehyde, which is a very powerful solvent for indigo, can be employed with good effect in many cases, especially for the quick and complete removal of indigo prior to making a qualitative examination of the topping or bottoming colour. Owing, however, to the tendency possessed by benzaldehyde to form condensation products with indigo which give a yellow tint to the wool, it is unsuitable for stripping when it is required to make tintometric estimations of the residual colour. For the latter purpose, the best extracting agent is cresol mixed with a certain proportion of a hydrocarbon of lower boiling point. 100 parts cresol (best commercial cresylic acid, 97-98%) with 30 parts of "solvent naphtha" of boiling point 125°-140°, or 75 parts of cresol with 25 parts of "turpentine substitute" or heavy petrol of boiling point 155°-170° have proved to be suitable mixtures. The extraction is effected in an *ordinary* Soxhlet extractor, which is provided with an air or water condenser. The sample, previously dried in a steam oven, is laid on a little loose wool and covered lightly with a further layer of loose wool, a thermometer being placed with its bulb in contact with the pattern. The proportion of hydrocarbon to cresol is so adjusted that the temperature of the extracting liquid round the pattern



does not exceed  $110^{\circ}$ , and is preferably about  $100^{\circ}$ – $105^{\circ}$ . The lower the temperature at which the extraction of the indigo can be effected, the less the danger of disturbing the concomitant dyestuffs. Care should be taken not to continue the extraction after the indigo has been completely removed or a loss of residual colour may occur. Carried out with care this method of separation seems capable of almost universal application, and the only cases in which the original depth of the bottoming or topping colour was not obtained were with Soluble Blues, Picric Acid, and redwoods, in which there was strong evidence that the bottom dye had already been partly removed in the indigo vat.

The behaviour of the four solvents selected towards a variety of colouring matters dyed upon wool in conjunction with indigo is shown in the following table. The minus sign indicates that the colour is stripped, the plus sign that it is not affected or only slightly, and the sign (+ –) that it is partially removed. Those dyes marked by an asterisk are changed in shade to violet.

Apart from the above-described use of extraction methods for estimating

Name of colouring matter	Acetic acid	Pyridine	Benzaldehyde	Cresol mixture
Sulphoncyanine 5R extra and GR (By.)	–	–	+	+
Brilliant Alizarin Blue R (By.)	+ –	+ –	+	+
Topping Violet RTN (B.A.S.F.)	+	–	+	+
Indocyanine 2R (Ber.)	+	+	+	+
Erio Fast Purple A (Gy.)	+	–	+	+
Fast Acid Violet R (M.L. & B.)	+ –	+ –	+	+
Chrome Blue A (B.A.S.F.)	+	+	+	+
Palatine Chrome Blue 2B (B.A.S.F.)	+	+	+	+
Hæmatine crystals	–	+	+	+
Eriochrome Asurol B (Gy.)	–	+	+	+
Omega Chrome Cyanine B (Sz.)	+	+	+	+
Alizarin Blue Black B (By.)	+ –	+	+	+
Alizarin Blue SW (B.A.S.F.)	+ –	+	+	+
Sulphon Dark Blue 2B	–	–	+	+
Wool Fast Blue BL (By.)	+ •	–	+	+
Indochromine 2R conc. (Sz.)	+ •	+	+	+
Cudbear on bichromate	–	–	+ –	+
Azofuchsine	–	–	+	+
Alizarin Red IWS (M.L. & B.)	+ –	+	+	+
Sanderswood and bichromate	–	+ –	+ –	+ –
Camwood and bichromate	–	+ –	+ –	+ –
Barwood and bichromate	–	+ –	+ –	+ –
Omega Chrome Red B	+	–	+	+
Gallein paste	–	+	+	+
Gallocyanin	–	+	+ –	+
Alizarin Cyanine 3R	–	+	+	+
Lanacyl Violet B (Cass.)	+	–	+	+
Soluble Blue	–	–	–	+ –
Acid Chrome Blue 2R (By.)	+ •	+ –	+	+
Eriochrome Blue BR (Gy.)	+	–	+	+
Acid Violet 4BRS (Sz.)	+	–	+	+
Omega Light Violet R (Sz.)	+	–	+	+
Myrabolans and iron	–	+	–	+
Fustic and bichromate	–	+	+	+
Picric acid	–	–	+	+ –
Logwood and bichromate	–	+	+	+
Indigo extract	+	–	+	+
Eriochrome Red BR (Gy.)	+	–	+	+

quantitatively the relative proportion of the colour depth which is due to indigo, they afford a ready means of roughly gauging the amount of the topping or bottoming colour, and of testing it for fastness, which should be of great service to the merchant and dyer. Moreover, after the removal of the indigo, the concomitant dyestuff or dyestuffs can be easily identified by making use of a scheme of qualitative analysis such as that of Green, for although the identification of other dyestuffs in presence of indigo is a difficult and often impossible task, this becomes a fairly straightforward matter when the indigo has been removed. Thus, for example, in investigating a navy blue cloth supplied to a London railway company, it was easily shown that it consisted of indigo topped with a mixture of Eriochrome Azurol and Logwood. In cases in which more than one topping or bottoming colour has been employed, an indication may often be obtained by comparing the residual colours left by different stripping agents. The testing of the residual colour for fastness to washing, light, etc., may frequently be an important factor in judging the quality of a navy blue shade, as it is obvious that the fastness of the concomitant dyestuff should also be taken into account together with the percentage of indigo present.

In order to submit to further test the general applicability of the stripping method for the quantitative estimation of the "percentage colour effect due to indigo," a number of official and Government cloths (Series V in foregoing tables) were subjected to independent examination by two observers, one of whom (Frank) employed cresol mixture, whilst the other (Lloyd) used dry pyridine for removing the indigo. In each case the tintometric readings of the stripped patterns were all observed together, and the units of total colour converted into indigo equivalents by reference to a curve which was constructed at the time. The results are shown in the following table:

Number of sample	Indigo found by analysis (= A)		Indigo equivalent of residual colour (= B)		Percentage colour-effect due to indigo ( $= \frac{100 A}{A + B}$ )	
	Frank	Lloyd	Frank	Lloyd	Frank	Lloyd
72	2.35	2.52	0.55	0.72	80	77
73	2.54	2.59	0.20	0.22	92	92
74	4.18	4.18	0.68	0.72	86	85
75	3.23	3.35	0.68	0.55	83	86
76	3.23	3.12	0.30	0.36	91	90
77	3.0	3.25	0.65	0.65	82	83
78	4.23	4.20	0.30	0.32	93	93
79	2.54	2.60	0.75	0.48	77	84
80	2.82	2.90	0.60	0.62	81	82
82	2.91	3.03	0.40	0.32	88	90

It appears from these results that the maximum error of the process is about 7% and with practice would not exceed 5%.

A few observations are desirable with regard to the use of the tintometer. The best form of this is the "three aperture" instrument, with which the

pattern can be placed in the central opening whilst matching glasses are used on either side of it. With this form of instrument it is easy to confirm the results arrived at, by varying the matching glasses on one side, and differences in depth of shade are more apparent than with the duplex tube. The readings should be made with a good north light coming from the front, and the instrument should be placed upright or at an angle not less than  $70^\circ$  to the horizontal, taking care, however, that there is no top light to cast a shadow on the pattern.

The following additional observations have been made in the course of the above work:

(1) If ordinary wool and chromed wool are dyed together in a vat, practically the same percentage of indigo is absorbed by each.

(2) Although the chroming of indigo dyed wool generally causes some loss of indigo, the after-chroming of a topping dyestuff does not appreciably affect the indigo unless the temperature or amount of chrome is too high.

(3) Many dyestuffs used for bottoming purposes, whether acid or chrome colours, cause the wool to absorb more indigo from the vat than does untreated wool under the same conditions.

(4) There is no difference in the final tintometric value when, for example, a red colour is topped on indigo dyed material, or the indigo topped on the red dyed material, provided that the amount of indigo and red colouring matter are the same in each case.

**Analysis of Indigo Containing Starch.**—W. Thomson<sup>1</sup> states that Rawson's permanganate process is not applicable for the direct estimation of indigo containing starch, and suggests that such samples be previously heated to  $90^\circ$  with a 4% solution of hydrochloric acid, filtered and washed with hot water and dried before sulphonation.

These observations were corroborated by Frank and Perkin.<sup>2</sup>

#### ERRATA IN VOL. V.

Page 116, line 7 from bottom, insert comma after "dyeing." Line 8 from bottom, italicise "colour bases." Line 4 from bottom, for "unsoluble" read "insoluble."

Page 117, line 16 from top, italicise "neutral dyestuffs."

Page 119, line 6 from bottom, for "513" read "435."

Page 120, line 6 from top, for "indamines" read "indamine."

Page 124, line 21 from top, between "and" and "much" insert "is."

Page 131, line 8 from top, for "Dinitroresorcniol" read "Dinitroresorcinol."

Page 131, last line, for "dilutiou" read "dilution."

Page 135, 2 lines from bottom, for "ChyrsoIn" read "ChrysoIn."

Page 135, line 9 from top, replace "and" by "only."

Page 136, line 9 from top, for "wth" read "with."

Page 137, second footnote, for "Polyp" read "Polyt."

Page 138, space 3 from bottom, replace "Ocange" by "Orange."

<sup>1</sup> *J. Soc. Dy. and Col.*, 1911, 49.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1912, 372.

- Page 140, line 2 from bottom, for "Ponccau" read "Ponceau."
- Page 147, line 13 from top, for "diamine nitrazole" read "diaminogen."
- Page 148, space 5 from top, delete "R salt." Space 7 from top, for "from G salt. Isomers from R salt" read "From R salt. Isomers from G salt."
- Page 148, space 10 from top, for "R salt" read " $\beta$ -naphtholsulphonic acid S."
- Page 149, space 4 from bottom, for "phenatidine" read "phenetidine."
- Page 152, space 8 from bottom, for "trisulphonic" read " $\beta$ -naphtholtrisulphonic."
- Page 160, first line, after "solution" insert comma.
- Page 164, lines 18 and 19 from top, for "salt R" read "R salt."
- Page 165, lines 1 and 2 from top, formula should be " $C_{10}H_8(NaSO_3)_2.N_2.C_{10}H_8.N_2.-C_{10}H_8$ ."
- Page 165, line 13 from top, for " $\beta$ -naphthol- $\gamma$ -disulphonic acid" read " $\beta$ -naphthol-disulphonic acid G."
- Page 176, line 5 from top, for "G" read "K."
- Page 178, space 4 from bottom, for "From sulphanilic and naphthionic acid" read "From *m*-aminobenzenesulphonic and naphthionic acids."
- Page 180, space 3 from bottom, formula for Benzo-grey should be
- $$\begin{array}{l} C_6H_4 - N = N - (2)C_6H_5 \left\{ \begin{array}{l} (1)OH \\ (4)CO_2Na \end{array} \right. \\ | \\ C_6H_4 - N = N - (4)C_{10}H_8(1) - N = N - (2)C_{10}H_8 \left\{ \begin{array}{l} (1) OH \\ (4) SO_2Na. \end{array} \right. \end{array}$$
- Page 186, third space from bottom, formula for Rouge M, for " $C_{10}H_8$ " read " $C_{10}H_6$ ."
- Page 198, space 4 from bottom, for "From  $\gamma$  acid" read "From D acid."
- Page 202, replace "the last named dye" by "Benzopurpurin 4B."
- Page 203, line 9 from top, for " $\alpha$ -naphtholdisulphonic acid" read " $\beta$ -naphtholdisulphonic acid."
- Page 203, line 15 from bottom, for "2" read "two." Line 11 from bottom, for "1" read "one."
- Page 204, line 14 from top, for "or stannous" read "of stannous."
- Page 204, line 14 from bottom, for " $C_{10}H_8(NH_2)OH$ " read " $C_{10}H_6(NH_2)OH$ ."
- Page 206, first space at top, " $C_6H_4:(N_2H_2)$ " should be " $C_6H_4:(NH_2)_2$ ."
- Page 207, line 8 from top, for "Leibermann" read "Liebermann."
- Page 208, line 19 from top, for "-acetal-" read "-acetyl-."
- Page 213, line 4 from bottom, between "and" and "used" insert "when."
- Page 215, line 10 (heading), omit full stop after "Paste."
- Page 216, table in centre of page belongs to footnote which it should follow.
- Page 226, line 12 from top, for "mordan" read "mordant."
- Page 442, line 16 from bottom, for "simple" read "similar."
- Page 444, line 16 from top, for "being" read "is."
- Page 448, line 26 from top, for "becomes coloured dilution" read "becomes coloured on dilution."
- Page 451, L. H. S. third line, for "saffranine" read "safranine."
- Page 452, L. H. S. third line, for "saffranine" read "safranine."
- Page 453, L. H. S. at bottom, delete "(cerumn)."
- Page 453, line 6 from bottom, for "turn to a yellow" read "turn it yellow."
- Page 454, right-hand bottom corner, in both cases for "saffranine" read "safranine."
- Page 464, line 9 from bottom, for "Is" read "If."
- Page 476, line 14 from top, for "value" read "loss," after which insert semicolon.
- Page 480, first line, after "Blue" insert "is."
- Page 487, line 1, delete comma after "spirit."
- Page 488, line 17 from bottom, after "dyed" insert "with."
- Page 490, italicise names of reagents.

Page 516, line 1, for "OR VEGETABLE" read "ON VEGETABLE."

Page 543, line 7, for " $\text{HNO}_{12}$ " read " $\text{HNO}_2$ ."

Page 569, second and third spaces, for "Fbre" read "Fibre."

Page 573, second space, for "Decolurised" read "Decolourised" and for "Substanive" read "Substantive."

Page 574, third space, for "Diamined" read "Diamine."

Page 592, heading of column, for "Soluton" read "Solution."

Page 598, space 10, for "Sapphiroll" read "Sapphirol."

Page 611, sixth space, delete "continued."

Page 615, space 3, column 10, for "become" read "becomes."

# COLOURING MATTERS IN FOODS.

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By ALBERT F. SEEKER, B.S.

Since the publication of Vol. V of the present edition the efforts of food analysts have been directed mainly towards isolating the colours from food in a condition to permit of their identification, this being a result of the tendency of governmental regulations to tolerate the use of certain colours provided they are harmless and do not conceal inferiority or otherwise promote fraud. In a comprehensive work "*Coal-tar Colours Used in Food Products.*" B. C. Hesse<sup>1</sup> has discussed the subject from a commercial, scientific and administrative standpoint, giving a list of the dyes that have been used, the commercial requirements of such colours, a compilation of records and work concerning the physiological effect of the dyes, legal enactments in various countries and recommendations by associations and individuals as to their use, and requirements concerning the degree of cleanliness and purity of the dyes to be employed for this purpose, together with methods for their analysis, the methods given being applicable only to the dyes themselves.

The limitation of the number of dyes permitted in food has resulted to a certain extent in increasing the use of mixtures of dyes to produce the desired shades and for this reason it has become of the greatest importance to modify analytical procedure so that such mixtures may be recognised when present and the individual colours properly separated and identified. An admirable systematic procedure to attain this end has been devised by W. E. Mathewson for the A. O. A. C.<sup>2</sup> In this method the basic dyes are first removed from alkaline solution by shaking with ether, the aqueous mixture being then strongly acidified and shaken with amyl alcohol to remove most of the acid colours. Light Green S. F. Yellowish and similar strongly sulphonated triphenylmethane dyes which may still remain in the aqueous liquid are removed by proper treatment with dichlorhydrin. Upon washing the separated organic solvents with successive small portions of water or with appropriate alkaline or acid solutions a separation of the constituent colours can in many cases be accomplished. The substance of Mathewson's method is as follows:

**Separation of Colours by Means of Immiscible Solvents.**—If the substance under examination is a solid insoluble in water, reduce it to a fine state of division and secure a solution of the colouring matter by macerating in

<sup>1</sup> *Bulletin 147, Bureau of Chemistry, U. S. Department of Agriculture.*

<sup>2</sup> *Bulletin 162, Bureau of Chemistry, U. S. Department of Agriculture.*

dilute (50–70%) alcohol made slightly alkaline with ammonia, or by a suitable method indicated on pages 649 to 663, Vol. V, under the heading of the respective food products. Dissolve the soluble substances in water. When working with solid samples advantage should be taken of any possible mechanical separation of portions coloured with different dyes. After a solution of the colour has been obtained, remove alcohol from the liquid by evaporating on a steam-bath, avoiding the formation of a dry residue by adding water.

*A. Separation of Basic Colours.*—Test a small portion of the dealcoholised liquid for basic colours by rendering alkaline with sodium hydroxide and shaking with ether. Separate the ether layer and shake it with dilute acetic acid. A coloured ether or acetic acid layer indicates the presence of a basic colour. In this case make the entire aqueous solution alkaline with sodium hydroxide and extract it with several successive portions of ether until the basic colour is all removed, as indicated by the fact that practically no colour is developed on shaking some of the last ether extract with dilute acetic acid. Shake the combined ether extracts with successive small portions of water, and finally with dilute acetic acid until colour is no longer extracted, keeping separate the aqueous layer obtained after each washing of the ether. A difference in the colour, fluorescence or other characteristic of these successive fractional washings indicates the presence of more than one basic dye. Combine the fractions containing the chief amount of each colour, make alkaline as before, shake out with ether, and subject the ether layer to fractional washing with water or dilute acetic acid as the case requires. By re-fractionating in this way some of each of the constituent basic dyes of a mixture may usually be obtained in a pure state and may be identified as indicated in Vol. V, p. 648. A tabular scheme showing the manner in which the dyes are removed from ether by the fractional washing is given on page 452.

*B. Separation of Acid Coal-tar Colours and Some of the Natural Colours.*—  
(a) Treat the original aqueous solution from which the basic dyes have been removed with half its volume of concentrated hydrochloric acid and shake with successive portions (about 25 c.c. each) of amyl alcohol until no more colour seems to be extracted. Not more than two or three extractions are usually required and the total volume of the amyl alcohol used need not exceed 50 to 75 c.c. Wash the combined amyl alcohol extracts with a little hydrochloric acid (1 part of strong acid and 2 parts of water) to remove sugar and similar impurities, the washings being rejected. Now shake the amyl alcohol with successive portions of water, the amount used each time being about half the volume of the amyl alcohol, until the washings are perfectly neutral, the water layer after each washing being run into a separate container. Eight or ten fractions will usually be obtained. Dilute the amyl alcohol with 1 or 2 volumes of gasoline or petroleum ether and shake out once or twice with water and finally with a very dilute sodium hydroxide



solution, the aqueous layers in this case also being kept each in a separate container. As in the case of the basic colours above described the presence of different dyes is indicated by a difference in colour, etc., of the successive fractional washings. Account must be taken at this point of the fact that some colours like Naphthol Yellow S. are more or less completely decolourised by mineral acid and also that many others are so modified in colour by different degrees of acidity that treatment of a small portion of each fraction with sodium bicarbonate is necessary to determine whether or not a colour or a mixture of colours is in fact present.

If a sufficient separation of the acid colours has not been effected by this treatment, combine the fractions containing the chief amount of each colour, acidify, shake up with amyl alcohol, separate the latter and wash with water (or hydrochloric acid of suitable strength) in the manner previously described. With the colours coming out last, use ether or petroleum ether instead of amyl alcohol in this purification. Occasionally in washing the amyl alcohol solution the liquids do not separate readily. In this case the mixture may be poured into a beaker and warmed, or hot water may be used. It is better, however, to use a centrifuge in breaking the emulsion because with hot mixtures a higher degree of acidity is required in order to extract the dye. Care should be taken at all times to keep the volumes of solutions as small as possible. The tabular scheme on page 452 shows the manner in which the acid dyes are removed from amyl alcohol by fractional washing. Identification of the separated colours is effected as indicated in Vol. V, p. 648.

The *natural colouring matters* archil (unsulphonated), turmeric, and saffron are taken up by the amyl alcohol when shaken with this solvent as under B(a) and are not removed until, after dilution with gasoline, the mixture is shaken with dilute sodium hydroxide. Separate the alkaline solution, acidify slightly with hydrochloric acid, and shake out the colour with amyl alcohol. Evaporate the amyl alcohol extract to dryness on a steam bath and test the residue for identity of the colour as indicated on page 632, *et seq.*, of Vol. V. Cochineal and Persian berry are also taken up by the amyl alcohol under B(a) but are gradually removed by the washings with water and completely by the fraction obtained after dilution with gasoline. To obtain a comparatively concentrated solution of these two colours for purposes of identification unite the fractions containing them, acidify with hydrochloric acid and shake with amyl alcohol. Separate the latter, dilute with 2 volumes of gasoline and shake with a little water. The colour passes into the water layer and may be identified as indicated on page 632, *et seq.*, of Vol. V. Some of the natural colouring matters are rendered much paler by acids and may be overlooked in the fractional washings. The acid solutions of most natural colours are deepened in tint by adding stannous chloride, while most of the commonly used coal-tar colours are decolourised, and it is therefore advisable to test a few drops of the strongly coloured fractions with this reagent.

(b) The original mixture from which the basic colours have been removed with ether, and most of the acid colours with amyl alcohol which may appear perfectly colourless, may still contain Light Green S. F. Yellowish and some other dyes. Make the mixture slightly alkaline with sodium carbonate or ammonia and then acidify slightly with acetic acid. Shake once or twice with amyl alcohol to remove any Guinea Green, Methylene Blue, etc., that may be present. Then extract with one or two small portions of dichlorhydrin which removes Light Green S. F. Yellowish and similar strongly sulphonated triphenylmethane greens. Separate the dichlorhydrin, dilute with double its volume of benzene and wash out the colour with water.

**Outline of the Manner in which the Coal-tar Colours Behave when Shaken with Various Solvents under Conditions Given in the Above Scheme.**<sup>1</sup>—In the colour separations as described, any given dye will in general, appear in several washings and the table given below is therefore only designed to show where the maximum amount will come out. The numbers refer to the dyes as listed in Green's edition of Schultz and Julius, *Systematic Survey of Organic Colouring Matters*, 1904, and are identified by name on page 641 of Vol. V, this edition, with the six exceptions here given.

2—Victoria Yellow.  
3—Martius' Yellow.

7—Aniline Yellow.  
62—Palatine Red (B).

491—Wool Green S (B).  
602—Nigrosin Soluble (A).

**A. Basic dyes.** Extracted by ether from strongly alkaline solutions. (Extracted only in small amount, perhaps with decomposition: 650.)

- (1) Readily removed from ether by washing with water: 448, 584.
- (2) More or less slowly removed by water, quickly by acetic acid: 425, 427, 428, 451, 452, 504, 655.
- (3) Not removed by water, fairly readily removed by acetic acid: 17, 18, 197, 201.
- (4) Not removed by acetic acid, fairly readily removed by hydrochloric acid (oil-soluble colours): 7, 16.
- (5) Not removed by hydrochloric acid (oil-soluble colours): 11, 49, 60.

**B. Acid dyes.** Not extracted by ether from alkaline solution.

**a. Extracted by amyl alcohol from strongly acid solutions.**

- (1) Removed in first washings of amyl alcohol extract, acidity high: 8, 9, 89, 108, 692.
- (2) Removed at lower acidity, but usually above fourth normal: 94, 106, 107, 602.
- (3) Removed at rather low acidity: 14, 53, 188, 480.
- (4) Removed at very low acidity, but before washings are neutral. Like preceding acid colours, not extracted by amyl alcohol from 5% sodium chloride solution.
  - (a) Removed from strongly acid solution by amyl acetate: 4.
  - (b) Not readily removed by amyl acetate: 55, 56, 62, 64, 65, 84, 103, 105, 139.

<sup>1</sup> W. E. Mathewson, *loc. cit.*

- (5) Removed by water from the practically neutral solvent, most readily after addition of petroleum ether.
  - (a) Not completely extracted by amyl alcohol from 5% sodium chloride solution: 146, 169, 667.
  - (b) Almost completely extracted:
    - (1) Extracted by 5% sodium carbonate solution from amyl alcohol: 85.
    - (2) Not readily extracted: 13, 86, 95, 97, 101, 137, 329 (464, 468, 433).
- (6) Removed by diluted sodium hydroxide solution from the amyl alcohol-petroleum ether mixture. Readily extracted by ether from acid solutions: 2, 3, 269, 510, 512, 516, 517, 518, 520, 523.
- b. *Not extracted from the strongly acid solution by amyl alcohol.*
  - (1) (Decomposed: 398.)
  - (2) (Dye separates as a precipitate but is extracted by dichlorhydrin: 240, 602.)
  - (3) After adding ammonia until nearly neutral:
    - (a) Readily extracted by amyl alcohol: 433 464, 468 (650).
    - (b) Not readily extracted by amyl alcohol:
      - (1) Extracted by dichlorhydrin: 434, 435, 440, 491.
      - (2) Not readily extracted by dichlorhydrin: 462.

**Separation of the Seven Colours Permitted in the United States.**—In the routine examination for colours as described above all the permitted dyes excepting Light Green S. F. Yellowish will be extracted by the amyl alcohol under B (a). Upon washing the amyl alcohol with water the different colours will appear in the washings in the following order: Indigo Carmine, Amaranth, Ponceau 3R, Naphthol Yellow S, Orange I, and Erythrosin. The separation of the Indigo Carmine and Amaranth by the fractional washing is quite sharp, that of Ponceau 3R and Naphthol Yellow S not so much so, while the great bulk of Orange I and Erythrosin remains in the amyl alcohol until after dilution with gasoline. The combined fractions containing the bulk of the Naphthol Yellow S and Ponceau 3R are treated with about one-eighth their volume of concentrated hydrochloric acid and shaken with two or three successive portions of amyl acetate which removes the Naphthol Yellow S leaving the Ponceau 3R in the aqueous layer. Strongly acidify the separated aqueous layer and shake the colour into a little amyl alcohol. Wash the amyl alcohol with a little *N/4* hydrochloric acid, dilute with 2 volumes of gasoline and shake out the colour with a little water. Wash the amyl acetate containing the Naphthol Yellow S once with dilute hydrochloric acid (1 volume of concentrated hydrochloric acid and 9 volumes of water) and then remove the colour by washing with water. Orange I is removed from the original amyl alcohol extract by diluting with gasoline and washing with water. Any trace of Erythrosin can be removed from these washings by acidifying with acetic acid and shaking with ether. The Erythrosin re-

maining in the amyl alcohol-gasoline is removed by shaking with dilute sodium hydroxide solution. It may be purified by acidifying the alkaline solution and shaking with ether. Upon shaking the ether extract with dilute ammonium hydroxide the colour passes into the aqueous layer. Light Green S. F. Yellowish remains in the original aqueous layer after shaking the strongly acid solution with amyl alcohol as in B(a). It is removed after neutralising most of the free acid, by shaking with dichlorhydrin as in B(b<sub>3</sub>). After diluting with benzene the colour is removed by washing with water.

The three colours Ponceau 3R, Naphthol Yellow S, and Orange I can be most readily separated by treating their aqueous solution with one-fourth its volume of sodium chloride solution (250 grm. per 1,000 c.c.) and shaking with one or two separate portions of amyl alcohol which removes the Orange I. Wash the amyl alcohol with 5% salt solution to remove any Yellow or Ponceau, and then two or three times with 5% sodium carbonate solution. The Orange I passes into the sodium carbonate solution leaving any Orange II, Crocein Orange, etc., that may be present in the amyl alcohol from which they may be removed by diluting with gasoline and shaking with water. Treat the combined salt solutions from which the Orange has been removed with one-tenth to one-fifth their volume of concentrated hydrochloric acid and shake with two or three successive portions of amyl acetate which takes up the Yellow. Remove the colour from the amyl acetate by washing with water. Shake the salt solution containing the Ponceau with amyl alcohol, separate the solvent, wash once with a little water, dilute with gasoline, and shake out the colour with a little water.

The solution of Ponceau 3R as obtained above should give a deep purplish-red precipitate on treatment with a few drops of barium acetate solution all of the colour being precipitated. Ponceau 2R also gives a precipitate under these conditions but its colour is carmine red. Amaranth can be distinguished from the Ponceaus and Fast Reds by its behaviour in acid solution when shaken with amyl alcohol. A dilute solution of the colour in *N*/4 hydrochloric acid when shaken with an equal volume of amyl alcohol will retain most of the Amaranth in the aqueous layer, Ponceau 3R on the other hand passing into the amyl alcohol. Indigo Carmine is not readily taken up from slightly acid solutions by dichlorhydrin which distinguishes it from common blue and green triphenylmethane and azin dyes.

**Read's Test for Detecting Colour in Tea.**<sup>1</sup>—This test has the advantages of simplicity and ease of manipulation as well as being capable of detecting smaller amounts of pigment than the methods given in Vol. V. Place about 25–50 grm. of tea in a sieve having 40 to 60 meshes to the inch and shake over a piece of white paper. If the tea is tightly rolled it should be slightly crushed, either before putting into the sieve or by rubbing it against the latter. Drag a spatula or the blade of a case knife flat side downward over the paper crushing the dust between the blade and the paper. A

<sup>1</sup> E. A. Read, Vol. 18, *Orig. Communications, 8th Intern. Congress App. Chem.*, p. 301.

little pressure applied by the finger to the end of the blade will be necessary to secure the proper crushing or streaking effect. Any particles of pigment in the dust will be revealed by a coloured streak on the white paper. If black unglazed paper be used white facing pigments can be detected in the same way by the appearance of white streaks. A lens with a magnification of 8 to 12 diameters is useful in detecting the smaller streaks. Observation of the streaks must be made in bright daylight, sunlight being desirable.

The *character of the pigments* present may be determined as follows: A black glossy streak indicates carbon. A blue streak may be due to prussian blue, ultramarine or indigo. Treat the colour either directly on the paper or after transferring to a microscopic slide, with a drop of 40% sodium hydroxide solution. Prussian blue will become yellowish-brown; indigo or ultramarine will remain unchanged in colour. Treat another portion of the streak with 10% hydrochloric acid. The blue colour of ultramarine is discharged; indigo remains unchanged. A yellow streak may indicate turmeric. This becomes bright red upon treatment with a mixture composed of concentrated hydrochloric acid saturated with boric acid. Concentrated sulphuric acid also turns turmeric bright red.

#### ERRATA IN VOL. V.

Page 636, line 17 from bottom for "Tumeric" read "Turmeric."

Page 648, line 12 from bottom, for "435 to 438" read "460 and 489."

Page 668, line 3 from bottom, in table, for "naphthaline" read "naphthalene."

# PRINTING INKS.

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By JOHN B. TUTTLE.

**Historical.**—The first printing inks were made by incorporating lampblack with burnt linseed oil. Later to meet the requirements of new conditions of presses, paper, etc., other oils, such as rosin oil, mineral oil, the semi-drying oils, China wood oil, etc., were introduced, whilst gas black, bone black or ivory black, magnetic pigment, etc., replaced the original lampblack. Colour printing required a great variety of pigments, divided roughly into two classes, the inorganic pigments, and the coal-tar dyes and lakes.

**Composition.**—Printing inks may be divided into two parts: first, a vehicle, or varnish; and second, the pigments.

The composition of the vehicle is determined by the nature of the work for which the ink is intended. It may contain linseed oil, mineral oil, rosin oil, the semi-drying oils, China wood oil, certain bituminous substances, hard gums or resins such as kauri and copal, rosin (colophony), various potassium, sodium, calcium and aluminium soaps, and one or more of a large variety of driers.

The linseed oil used in printing inks is specially prepared for the purpose by one of two methods. The older method, still in use in preparing oil for engraving inks, consists in heating the oil in an open kettle, setting fire to the fumes, and allowing the oil to burn until the desired consistency, or viscosity, is attained. The second method is to heat the oil in an open kettle at about 300° without allowing the vapours to inflame. In both processes a number of grades are prepared by varying the length of time of heating.

The rosin is added to the vehicle either as such, or in the form of the calcium soap. The driers are usually lead, manganese or cobalt salts of organic acids. The other constituents of the vehicle are used without special treatment.

The pigments used will depend not only upon the colour desired, but also upon the class of work. For example, in printing with one colour an opaque pigment is necessary so that the colour of the paper will not show through the ink, whilst a translucent pigment is required in the three- and four-colour processes, where the secondary colours are obtained by superimposing the primary ones.

The principal black pigments are lampblack, gas black (or carbon black), bone black, and artificial magnetic oxide of iron. The inorganic



coloured pigments include Prussian blue,<sup>1</sup> ultramarine, chrome yellow (including all the various hues from pale yellow to scarlet), chrome green, vermilion, etc. The organic pigments include the various coal-tar lakes and dyes.

**Manufacture of Ink.**—The mechanical part of the manufacture of printing inks is quite simple. The vehicle is prepared according to the desired formula and then the pigments are added. There is usually a preliminary mixing in a mill containing broad revolving knives or paddles, after which the inks are ground in a grinding mill. This latter consists of three rolls which revolve at different speeds, the rear one slowest, the front roll fastest. The ink is fed between the rear and middle rolls, is carried around by the middle to the front roll, where it is automatically scraped off. The differential speed gives the grinding effect and reduces the pigment to the finest division possible. Many of the better grades of ink are ground a number of times before they are considered satisfactory.

**Analysis.**—There has been very little work published on the analysis of printing inks. The methods which are given below are taken largely from the article on this subject by J. B. Tuttle and W. H. Smith.<sup>2</sup> The general procedure consists in separating, by means of suitable solvents the inks into two parts, oils and pigments, and testing the separate parts for the constituents which are likely to be present.

For inks in which the vehicle is largely, if not entirely, mineral or rosin oils, petroleum ether will be found a very satisfactory solvent, but for general use where the composition is unknown, a mixture of 3 parts ethyl ether and 1 part benzene is to be preferred. The separation is best performed by centrifuging; the settling process consumes too much time to be practicable.

**Separation of Oil from Pigment.**—About 50 grm. of ink (avoiding the hard film which frequently forms on the surface) are placed in a weighed glass tumbler of about 300 c.c. capacity, a small amount of solvent added, and the whole stirred thoroughly until a homogeneous mixture is obtained. The glass is then filled with the solvent to within about  $\frac{1}{2}$  in. from the top, and the whole again stirred. It is next placed in the metal cup of the centrifuging machine and the space between the glass and metal cups filled with water in order to equalize the pressure of the liquid inside the glass during the centrifuging. Placing a rubber disc at the bottom of the metal cup has been found to materially lessen the danger of breakage during the operation. The metal cup and contents are then exactly counterbalanced most conveniently by either a second sample of the same ink or another sample of ink, and then both are placed in the machine. For web-press and flat-bed inks, 2,000 revolutions per minute for 10 minutes will suffice for a

<sup>1</sup> The term Prussian blue is here used to denote any of the iron cyanide blues, such as Milori, bronze, Chinese blues, etc., which may be used in printing inks. These names are applied more or less indiscriminately; the simplest procedure, therefore, is to use the better known term "Prussian blue" to cover all of them. Even if there were a standard nomenclature, it is doubtful if they could be identified after incorporation in a printing ink.

<sup>2</sup> *Technologic Paper No. 39, of the U. S. Bureau of Standards, "The Analysis of Printing Inks."*



complete separation. Where gas black has been used, it has frequently been necessary to run the machine at 2,600 to 2,800 revolutions per minute for 20 or 30 minutes before a satisfactory separation is secured. The clear liquid is decanted through a pleated filter into a glass bottle, a further quantity of solvent added, and the process repeated. Usually three treatments suffice to give practically complete separation of oil and pigment. The glass and contents are dried at about 90° and on cooling, reweighed. The increase in weight is the pigment, which is calculated as a percentage. The amount of pigment on the filter paper should be negligible if the centrifuging has been efficient.

This method will not always yield results of great accuracy. The errors, which vary in magnitude with different inks, are as follows:

Some of the dyes are soluble to some extent in the solvents, tending to give low results for pigment.

Hard gums may not be completely soluble, and thus part will remain with the pigment.

The hard scum (linoxyn) which forms on the surface of the ink after it has been exposed awhile, is difficultly soluble and remains with the pigment. This should be excluded in sampling, for if it is not done, a considerable error may be introduced.

Carbon black contains some particles so fine that it is impossible to cause them to settle, even in the centrifuge.

The net error of this separation is therefore the algebraic sum of these various errors.

**Analysis of the Oil.**—The oil fraction may contain any of the oils, etc., mentioned in the paragraph on the composition of inks. Bituminous substances are judged largely by colour, being a mixture of a number of different substances of varying chemical nature; the estimation of the total amount present is a matter of too much difficulty to justify the time required.

**Oil Constants.**—Estimating the oil constants, such as iodine number, saponification number, acid number, etc., does not give very reliable data regarding composition. If there were but two components, the proportion of each might be estimated at least approximately in this way, but with three, and sometimes more substances present, such methods are useless, even if the constants of the individual substances are well known.<sup>1</sup>

We are therefore forced to rely upon qualitative tests, supplemented by quantitative estimations of some of the more important constituents. The oil fraction of an ink is independent of the colour; therefore the separation given below is applicable to inks of all colours.

<sup>1</sup> The various linseed varnishes used in printing inks have widely varying constants and the estimation of these is a very difficult problem. Smith and Tuttle have shown (*Technologic Paper No. 37 of the U. S. Bureau of Standards*, 'The Iodine Number of Linseed and Petroleum Oils'), that slight changes in the method used in estimating the iodine number of the so-called "burnt" linseed varnishes will give widely varying results. It would seem an almost hopeless task to attempt to determine just which varnish has been used, and the difficulties become even greater when, as is frequently the case, two or more of them are used in the same ink.

It will be found convenient to regard the oil fraction as consisting of hard gums, rosin, unsaponifiable matter (rosin and mineral oils) and linseed oil.

**Hard Gums.**—The hard gums are difficult to estimate, the only method which has given any measure of satisfaction being that of McIlhiny.<sup>1</sup> This method depends upon the insolubility of hard gums in water and petroleum ether. The method is much better adapted for the analysis of paints than printing-ink varnishes, but it can be used for the latter to obtain some idea of the amount present.

**Unsaponifiable Matter.**—Sufficient of the solution from the separation of the oil and pigment to leave a residue of about 5 grm. is evaporated in a weighed beaker; 50 c.c. of normal alcoholic potassium hydroxide is added, the beaker covered with a watch glass, and heated on a steam-bath for several hours, being stirred frequently to assist saponification. When the latter is complete, the watch glass is removed and the alcohol distilled off. The residue is transferred to a separating funnel with successive portions of water, in all about 100 c.c. being used, and extracted with petroleum ether until no further oil can be removed. Four extractions are usually sufficient. The petroleum ether fractions are united in another funnel, washed with water until the wash-water is no longer alkaline, filtered into a weighed beaker, the petroleum ether distilled off and the residue dried at 95°, cooled and weighed. If this unsaponifiable matter is over 2%, it indicates the presence of something else than linseed oil and hard gums. The wash-water from the first two washings should be united with the water layer in the first separating funnel.

**Rosin.**—This unsaponifiable matter is tested for the presence of rosin oil. The most satisfactory method of testing qualitatively for this material is the Liebermann-Storch test, which consists in heating a small portion of the oil with 10 c.c. of acetic anhydride, allowing it to cool, and adding a drop of sulphuric acid of sp. gr. 1.63. A violet colouration indicates rosin oil. It is always best to carry out a control test at the same time with some pure rosin or rosin oil. The test is identical for the two materials.

If the test for rosin oil is positive, the alkaline aqueous solution which has been extracted with petroleum ether is made acid with hydrochloric acid (there is usually sufficient dye present from the ink to act as indicator), and the fatty acids which are thus liberated are extracted with successive portions of ethyl ether. These extracts are united, washed free from acid and salts and evaporated in a small beaker.

A quantitative determination of the rosin can be made either by the Twitchell method, which depends upon the separation of the esters of the organic acids, or by Gladding's method,<sup>2</sup> which depends upon the separation of the silver salts of these acids.

A very satisfactory method is Parry's modification of Gladding's method.<sup>3</sup>

<sup>1</sup> P. C. McIlhiny, *Chem. Eng.*, 1908, 8, 70; *Chem. Abs.*, 1908, 2, 2630.

<sup>2</sup> *Amer. Chem. Jour.*, 1881, 3, 416.

<sup>3</sup> Vol. IV, p. 73.

The fatty acids are dissolved in 20 c.c. of 95% alcohol, a drop of phenolphthalein added and then a strong solution of sodium hydroxide (1 part alkali to 2 water) until the reaction is just alkaline. The solution is heated for a few minutes, allowed to cool, and then transferred to a 100 c.c. stoppered graduated cylinder. The latter is filled to the 100 c.c. mark with ethyl ether, 2 gm. of powdered silver nitrate crystals are added, and the mixture shaken vigorously for 15 minutes, in order to convert the acids into their silver salts. When the insoluble salts have settled, 50 c.c. of the clear solution (containing the silver salts of rosin) are pipetted off into a second 100 c.c. cylinder, and shaken with 20 c.c. of dilute hydrochloric acid (1 acid to 2 water). The ethereal layer is drawn off, and the aqueous layer is shaken twice with ether. The ether extracts are united, washed with water, and the ether distilled off in a weighed beaker. The residue (rosin) is dried at 110° to 115°, cooled, and weighed. The results are calculated on the basis of the original weight of the oil.

The difference between 100 and the sum of the unsaponifiable matter (if over 2%) and the rosin, may be considered linseed oil.

### Analysis of the Pigment.

**Black Inks.**—A mixture of oil and black pigments will not give a pure dense black, owing to the various undertones of the pigments. Moreover, the public is accustomed, in printing, to accept as black what is really a blue-black. Practically all of the pigments from black inks will be found to contain more or less blue, either in the form of Prussian blue, or blue dyes and lakes.

**Ashing.**—The first step in the analysis of the pigment of a black ink is to ignite a weighed quantity in a porcelain crucible (platinum cannot be used on account of the lead which is usually present). The ignition should be performed at the lowest possible temperature required to obtain complete combustion. This precaution is general and applies to all inks. The loss on ignition represents lampblack, the carbon of the bone-black (should there be any present), aniline dyes, and undissolved oils and gums. Prussian blue is decomposed by heat, part of it being volatilized, the iron remaining behind as ferric oxide. The residue from the ignition contains any added mineral matter of the pigment, lead or manganese from the driers, ferric oxide from the Prussian blue, or ferric oxide added as such (the so-called magnetic pigment), calcium phosphate if bone-black is present, and alkali or calcium carbonates from the soaps present. All ignitions of pigment must be performed under a hood having a strong draught.

Prussian blue should be tested for qualitatively in the dry pigment. For this purpose, 1 gm. of pigment is moistened with 2 or 3 c.c. of normal alcoholic potassium hydroxide, heated on the steam-bath until the alcohol is removed, 5 c.c. of water added, and the insoluble matter filtered off. The

**Filtrate** is made acid with hydrochloric acid and filtered again if necessary. When ferric chloride is added a blue precipitate will be obtained if Prussian blue is present. Sometimes sufficient blue dye goes through the filtrate to obscure the indication. In this case the solution is again made alkaline and filtered. After filtration it is made acid with hydrochloric acid as before and then copper sulphate is added. The precipitate is filtered and washed thoroughly, and consists of reddish-brown copper ferrocyanide. It is advisable, in case of doubt, to add a small amount of Prussian blue to the pigment, and make a control test. The ash is analysed quantitatively for insoluble matter, lead, iron, manganese and calcium.

**Insoluble Matter.**—0.250 gm. of the ash is heated to dull redness in a porcelain crucible for a few minutes, cooled in a desiccator, and weighed. It is transferred to a 250 c.c. beaker, concentrated hydrochloric acid being used to dissolve any material that may stick to the crucible. About 25 c.c. of concentrated hydrochloric acid are added, the beaker covered with a watch glass, and after heating until as much as will go in solution is dissolved, the cover is removed, and the solution evaporated to dryness. The residue is moistened with a few drops of concentrated hydrochloric acid, 50 to 75 c.c. of boiling water added, and the solution is filtered, washing thoroughly with hot water. The filter paper and residue are ignited and weighed, and the product called "*insoluble matter*."

**Lead.**—50 c.c. of 10% sulphuric acid are added to the filtrate from the previous estimation and evaporated down until the solution fumes strongly. This is cooled, diluted carefully with about 100–150 c.c. of water and heated on the steam-bath until any basic ferric sulphate which sometimes separates is redissolved. The precipitate, containing the lead sulphate, is now filtered off. A small amount of lead sulphate will, in all probability, remain in solution, but inasmuch as the ash is seldom more than a few per cent. of the entire ink, and of this only a small amount is lead, the amount thus lost is negligible. The precipitated lead sulphate is dissolved in ammonium citrate or acetate, filtered from any insoluble matter, the filtrate made strongly acid with sulphuric acid, and the precipitated lead sulphate filtered off on a Gooch crucible, ignited and weighed. A platinum Gooch crucible with a platinum felt will be found extremely satisfactory. The insoluble matter from the ammonium acetate solution should be examined for calcium and barium.

Another method for the estimation of the lead is nearly to neutralise the acid present with sodium carbonate, saturate the solution with hydrogen sulphide, filter off the precipitated lead sulphide, dissolve it in fairly strong nitric acid and determine the lead as sulphate by adding sulphuric acid as above described. In this case solution in ammonium acetate is omitted. The former method is advantageous when qualitative tests show that there is very little manganese present, and it is desired to estimate only the iron. After the lead sulphate has been removed the solution obtained is in perfect condition for this estimation.

**Iron.**—The iron in the filtrate from the lead sulphate is reduced to the ferrous condition by passing the solution through a Jones reductor, and the ferrous sulphate titrated with a standard solution of potassium permanganate.

Iron is separated from manganese and other metals which may be present by precipitating with ammonium hydroxide, the precipitate being filtered off, redissolved in hydrochloric acid, reprecipitated with ammonium hydroxide and again filtered. It is now dissolved in hydrochloric acid, sulphuric acid added, and the solution evaporated until all the hydrochloric acid is removed; it is diluted and the iron estimated as before, with the Jones reductor. This method is rapid and accurate. Before adding ammonium hydroxide, if hydrogen sulphide has been used, the solution should be boiled until all the hydrogen sulphide is removed, and nitric acid added to oxidise the iron to the ferric condition.

**Manganese.**—Hydrogen sulphide is now passed into the ammoniacal solution from the iron precipitation. This is allowed to stand over night, and the precipitate, if there is any, is examined for manganese. Usually there is only a trace of manganese, insufficient to warrant a quantitative estimation. Should there be much manganese, the sulphide can be filtered off, and the quantitative estimation made by conversion into the pyrophosphate.

**Calcium.**—If it is desired to estimate the calcium, this can be done after filtering from the manganese sulphide. (If phosphates are present, as for instance, if bone-black is present, a basic acetate separation is required.) In either case, the lead should be separated by hydrogen sulphide. The filtrate from the manganese sulphide is heated on the steam-bath until the hydrogen sulphide is removed, ammonium hydroxide and ammonium oxalate are added, and the precipitated calcium oxalate is estimated either as calcium oxide or sulphate.

**Nature of the Pigment.**—The percentage of ash will be of great assistance in determining the nature of the pigment. Black oxide of iron is only slightly changed on heating, being completely oxidised to ferric oxide. Bone-black is composed largely of calcium phosphate, yielding the greater part of its weight as ash. The presence of any large amount of phosphoric acid will be sufficient evidence that bone-black has been used.

In the absence of black oxide of iron, we may assume that all of the iron in the filtrate is due to the Prussian blue. The percentage of  $\text{Fe}_2\text{O}_3$  in the ash, multiplied by the percentage of ash in the pigment, multiplied by the factor 1.53 will give roughly the amount of Prussian blue present. The factor 1.53 is obtained from the ratio  $\text{Fe}_7(\text{CN})_{18}$  to  $\text{Fe}_2\text{O}_3$ . It is purely theoretical and is probably low, but is sufficiently accurate for most purposes.

When the presence of oxide of iron is suspected, 1 grm. of pigment is wrapped in filter paper, and the dye extracted with alcohol, using for this purpose an extractor of the Wiley type, in which the material is extracted by the solvent at its boiling point. When all the dye has been extracted, the paper and contents are dried, and the nitrogen is estimated in the residue by

**the Kjeldahl method.** From the nitrogen thus obtained, the Prussian blue is calculated, using the factor 3.41. The  $\text{Fe}_2\text{O}_3$  present in this amount of Prussian blue is deducted from the total  $\text{Fe}_2\text{O}_3$  found in the ash. The remainder will be the percentage of iron from the magnetic oxide. The formula of the latter is theoretically  $\text{Fe}_3\text{O}_4$ , and the proper calculation should be made. This method for the estimation of Prussian blue depends upon the fact that the aniline dye is the only other material which may contain nitrogen. Instead of calculating the Prussian blue from the amount of iron present, it is estimated from the nitrogen remaining after the removal of the aniline dye. In this way both Prussian blue and magnetic oxide of iron may be estimated with reasonable accuracy.

**Dyes.**—Practically all the dyes which are used in black printing inks are soluble in alcohol, so that an approximate estimation can be made by extracting the pigment with this solvent. This method is the same as described in the preceding paragraph, the alcoholic solution being evaporated off in a weighed beaker, dried at  $90^\circ$ , cooled and weighed.

### Blue Inks.

A weighed quantity of pigment is ignited as under black pigments. The ash is analysed by the same process as before, determining only lead, manganese, and iron if the qualitative tests show that Prussian blue is present. The lead and manganese are reported as metallic driers, the iron is calculated as Prussian blue, and the remainder reported as mineral filler. The composition of the filler, as a rule, is of no consequence.

**Ultramarine.**—The presence of ultramarine will be shown by the blue colour of the ash. Hydrogen sulphide is evolved from the latter on the addition of hydrochloric acid. There is, unfortunately, no method for its quantitative estimation. In this case, the ash is reported after deducting the lead and manganese.

Soluble aniline dyes are estimated by extraction with alcohol as under black pigments.

### Red Inks.

**Vermilion.**—The most brilliant red mineral pigment is unquestionably vermilion (mercuric sulphide). Its price prohibits its use except in inks used for special purposes. It is very readily detected qualitatively by covering a small quantity of pigment with 4 or 5 c.c. of aqua regia, and heating gently. The solution is diluted with 5 volumes of water, filtered, and stannous chloride added to the filtrate. A grayish precipitate of mercury will be formed if vermilion is present. A very small amount can be readily detected by this test.

The quantitative estimation of vermilion, however, is much more difficult. One method is to dissolve the mercuric sulphide in aqua regia, and



after nearly neutralising the diluted solution, to precipitate the mercuric sulphide with hydrogen sulphide and weigh the precipitate on a Gooch crucible, observing all the precautions to eliminate sulphur which separates during the precipitation.

The following process has also been found of value: 1 grm. of the pigment is treated with a slight excess of ammonium sulphide. Sodium hydroxide is then added, whilst stirring. The beaker is placed upon the steam-bath, more alkali is added if necessary, until all the mercuric sulphide passes into solution. An undue excess of alkali should be avoided. The solution is allowed to cool, filtered, and the residue washed thoroughly. To the filtrate, sufficient ammonium nitrate to reprecipitate the mercuric sulphide is added, and it is then boiled to expel ammonia. The precipitate is allowed to settle, which takes but a short time, and the supernatant liquid decanted through a weighed Gooch crucible. The residual mercuric sulphide is boiled with a little sodium sulphite solution to remove free sulphur, and is then transferred to the crucible, where it is washed with hot water until it no longer reacts with silver nitrate solution. It is dried at  $110^{\circ}$  and weighed.

The distillation method, in which the mercury is absorbed by gold, and the various electrolytic methods will appeal to those who have had experience with them.

**Metallic Driers.**—The pigment is ignited and the ash analysed for lead and manganese. The remainder of the ash is reported as mineral filler.

### Green Inks.

The colouring matter may be chrome green, green lake or dye. Some of the darker shades are obtained by the addition of lampblack.

**Ash.**—The ash of the pigment is estimated as usual. Part of this ash is tested qualitatively for chromium. If present, the ash should be tested for the following substances: lead chromate, lead sulphate, lead oxide, barium sulphate, calcium sulphate, ferric oxide, and oxides of manganese.

**Sulphur.**—To estimate sulphur, 0.250 grm. of the ash and 5 grm. of a mixture of equal parts of potassium nitrate and sodium carbonate are fused in a porcelain crucible over a sulphur-free flame. The cooled mass is extracted with hot water and filtered. The filtrate is acidified with hydrochloric acid, heated to boiling, and 10 c.c. of 10% barium chloride solution are added. After standing over night, the precipitated barium sulphate is filtered off, ignited, and weighed as usual. The solution should be sufficiently acid to prevent any significant contamination of the barium sulphate with barium chromate.

**Barium.**—To estimate barium, the insoluble matter from the determination of sulphur, is dissolved in hydrochloric acid, the solution made nearly neutral with sodium carbonate, and hydrogen sulphide is passed into the solution until all the lead is precipitated. The lead sulphide is filtered



off, the filtrate heated to boiling, and 10 c.c. of 10% sulphuric acid are added. The barium sulphate is treated as directed under the determination of sulphur.

**Chromium.**—A fresh portion of ash is mixed with sodium peroxide, and fused in a nickel crucible. The cooled melt is dissolved in hot water and filtered. Carbon dioxide is passed into the filtrate, and the latter heated again on the steam-bath in order to precipitate any lead which may have been held up by the sodium hydroxide. Any insoluble matter which may separate is filtered off. The filtrate is made strongly acid with hydrochloric acid, potassium iodide added, and the liberated iodine titrated with a standard sodium thiosulphate solution. From the amount of thiosulphate used, the amount of chromium oxide present is calculated.

The two precipitates from the estimation of chromium are combined, and used for the estimation of lead, iron, manganese and calcium. They are dissolved off the filter paper with hydrochloric acid, the solution is nearly neutralised with sodium carbonate, and hydrogen sulphide passed into the solution. The precipitated lead sulphide is filtered off, dissolved in nitric acid, and estimated as sulphate as directed under black pigments. The filtrate from the lead sulphide is treated for iron, manganese, and calcium, as directed under black pigments. Usually only the iron is of sufficient importance to warrant a quantitative estimation.

It is difficult to give precise directions for calculating the results from the preceding estimations. To a large extent the analyst must use his experience in deciding the various questions as they arise. It is probably safe to assume that all of the chromium was originally present as lead chromate, and it should be so calculated. The iron oxide should be calculated as Prussian blue provided there is a positive qualitative test. Any barium present should be calculated as sulphate; if there is any question as to its being originally present as carbonate, the ash of the pigment is treated with very dilute hydrochloric acid, the solution filtered, and the filtrate tested for barium. Barytes is difficultly soluble in cold dilute hydrochloric acid. In the absence of barytes, the sulphur present is calculated as lead sulphate. The excess of lead over that required for the lead chromate and sulphate, may be considered as drier.

China clay may be present, either as an added part of the chrome green, or as the base of a green lake. Aluminium hydroxide is also used as a base for coal-tar lakes. In such cases, the unestimated portion of the ash should be reported as lake base or mineral filler.

Green dyes are estimated by extraction as usual. In the absence of chrome green, the pigment is ashed, and the ash analysed for lead and manganese only, the remainder being reported as mineral fillers.

If lampblack has been used to produce a dark shade of green, it can be tested for qualitatively by taking a small portion of the pigment, treating it with strong alkali, and filtering through a Gooch crucible, washing first with

hot water, and finally with moderately strong hydrochloric acid. Lampblack will show a black residue, which will disappear on ignition. No quantitative estimation has been developed for this material, and it is generally classed with the volatile constituents, which are then reported as aniline dye, lampblack, undissolved oil, etc.

### **Inks of Other Colours.**

The above classes represent the inks most used for ordinary work. If it is desired to test other colours, the general procedure would be simply to make qualitative tests for the pigments. The metallic driers present can be determined in the ash if so desired. References to the various text-books on this subject may be of assistance in suggesting what materials may be present.

### **Permanence to Light.**

With coloured inks, the question of importance is frequently not so much what dye or lake has been used, and how much, but how permanent it is. Exposure to light is the easiest method for determining this. This test is performed by making some streaks on white paper with the ink in question. These should be about  $\frac{1}{2}$  in. wide, and about 10 in. long. The film of ink should be as thin as it is possible to make it, and should correspond as nearly as possible to the thickness of the film of ink used in printing. The sheet is allowed to remain in a dark place for 24 hours to dry thoroughly, and is then divided into three parts. The middle section is exposed to direct sunlight until the colour changes, or until it is apparent that no change will take place, 50 to 75 hours being about the right length of time. The two outside sections are kept in the dark, for the purpose of comparison. After the exposure is completed, the strips are joined together in their original position, when it is possible to detect very slight changes in colour. A number of inks can be tested on the same sheet if so desired.

Another method for determining the relative permanency of different samples of the same colour has been suggested.<sup>1</sup>

Flat tints of each ink are printed as strongly as if they were to be part of a colour job. These tints should be about 5 in. by 7 in. in size. They should then be cut out to this size. A photometer scale is then made of five layers of fine tissue paper, each layer 1 in. narrower than the preceding. This will give five different thicknesses of tissue, each thickness representing a band 1 in. by 7 in. Across these, and about 1 in. apart, should be glued three strips of opaque black paper, 1 in. wide and 5 in. long, starting 1 in. from and parallel to one narrow edge of the tissue paper. The photometer thus made, and a printed sheet of the ink to be tested, are then put into a

<sup>1</sup> Private communication from Mr. H. R. Gaylord and Mr. Averill, of the State Institute for the study of Malignant Disease, at Buffalo, N. Y., through Mr. E. S. Moores of the U. S. Government Printing Office at Washington, D. C.

photographic printing frame which has a plain glass in the front of it. The whole is then exposed to the sunlight with an ordinary photographic printing-out photometer until the total exposure has reached a certain value on the photometer scale (usually the last number). When the printed sheet is taken from the frame, it will be found to be divided into three unfaded areas, corresponding with the three opaque black strips, and four faded areas, each divided into five 1-in. squares which have each received different amounts of light. By placing sheets of different printing inks of the same colour in the frame, and exposing to sunlight to the same photometer number, the relative permanency of the different inks can be seen at a glance. If desired, three inks may be tested at one time by cutting the flat tints into strips 2 in. wide and 5 in. long, and placing them in the frame so that each has an exposed and an unexposed area.

### Dyes and Lakes.

So far, little success has been met with in attempting to estimate the various coal-tar lakes used in printing inks. The soluble dyes may be removed by extraction, and the amount present estimated in this way. Some of these may be identified by the number and location of the absorption bands, using for this purpose the tables given by J. Formanèk in his book on "*Spektralanalytischer Nachweis Künstlicher Organischen Farbstoffe*."

### Special Tests.

The foregoing tests cover practically all the important components of the common inks. A few other tests might be made in case of trouble that cannot otherwise be located.

Volatile constituents in the ink can be determined by placing a weighed quantity in a shallow layer in a porcelain or glass dish and heating in an air-bath for 1 hour at 105°, cooling in a desiccator, and weighing. It is hardly necessary to take the precaution of drying in an inert atmosphere. These volatile constituents may be benzine, turpentine, benzene, etc.

Certain patents call for the use of sodium silicate (water glass) in the thickening of the oil. The alkaline nature of this substance would prohibit its use in the presence of blue dyes and Prussian blue. It will probably be found with the pigment, and is easily tested for by treating the pigment with boiling water, filtering off the undissolved material, and testing the filtrate with phenolphthaleïn. It can hardly be considered a desirable substance in printing inks.

### ERRATA IN VOL. V.

Page 675, line 4, for "Eisingallustintien" read "Eisengallustinten."

Page 698 (index) under "Knecht," for "stannous" read "titanous."

# INKS.

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By PERCY H. WALKER.

For the estimation of tannin in writing inks reference may be made to F. W. Hinrichsen (*Die Untersuchung von Eisengallustinten*, page 65) and R. Kempf (*Untersuchung über Eisengallustinten*, Mitt. Königl. Materials Prüfungsamt, 1913, 451).

# AMINES AND AMMONIUM BASES.

By W. A. DAVIS.

## Estimation of Ammonia and Trimethylamine.

K. Budai<sup>1</sup> suggests the following method to estimate trimethylamine and ammonia when present together. The aqueous solution of the hydrochlorides of the two bases is treated with excess of formalin, previously made neutral to phenolphthalein and is then titrated with *N*/10 sodium hydroxide in presence of phenolphthalein; the number of c.c. used (*x*) corresponds with the ammonia.



The solution is now diluted with a large quantity of water, made strongly acid with sulphuric acid and concentrated to one-third of its volume over a bare flame. The hexamethylenetetramine produced by the action of the formaldehyde on the ammonium salt is in this way hydrolysed into ammonia and formaldehyde. The solution is now made alkaline and distilled, the vapours being collected in excess of *N*/10 acid, the excess of acid subsequently remaining being titrated. From this titration the number of c.c. (*y*) of the *N*/10 alkali corresponding with the ammonia and trimethylamine is ascertained, and hence *y* − *x* gives the value corresponding with the trimethylamine.

## Hydrazine.

For the properties of hydrazine nitrate, see W. R. E. Hodgkinson.<sup>2</sup> This salt melts at 70° and may be kept at 100° for a long time without change. When heated at 200° *in vacuo* the gases evolved correspond with decomposition according to the equation:  $4\text{NH}_2\text{NH}_2, \text{HNO}_3 = 5\text{N}_2 + 2\text{NO} + 10\text{H}_2\text{O}$ . Heated in a closed vessel the nitrate decomposes violently but under ordinary pressure merely burns rapidly. Contact with many oxidising agents, for example, permanganates, chromates, peroxides, causes inflammation. A solution of the nitrate does not act appreciably on zinc, cadmium and magnesium (which are, however, rapidly dissolved by cold saturated ammonium nitrate solution). Zinc, cadmium and copper added to the fused salt cause a flaming decomposition of the salt at slightly above 70°. Fragments of ordinary commercial cube cobalt or nickel added to the fused salt cause a violet explosion, but this behaviour is not shown by the

<sup>1</sup> *Zeit. physiol. Chem.*, 1913, 86, 107.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1913, 32, 519.

same metals that have been melted and worked into wire, nor by these metals when prepared by reducing the oxides in hydrogen. In the latter case the metal is only slightly oxidised when added to the fused nitrate, which burns away rapidly.

According to Sommer<sup>1</sup> hydrazine may be estimated in presence of nitrous acid by titrating with iodine after adding bicarbonate, and the amount of nitrous acid may then be found by adding potassium iodide, displacing oxygen by carbon dioxide, adding dilute sulphuric acid and titrating with thiosulphate.

### Estimation of Antipyrine.

W. O. Emery and S. Palkin<sup>2</sup> give the following methods of estimating antipyrine either alone or in presence of other substances.

I. *Alone or free from substances yielding a derivative capable of being extracted with chloroform.*

A quantity of the sample containing not more than 0.25 gm. of antipyrine is dissolved in 20 c.c. of water and treated with 5 c.c. of alcohol-free chloroform, 0.5 gm. of sodium hydrogen carbonate and a slight excess of iodine (15–20 c.c. of *N*/5 solution); after vigorously agitating at intervals during 5 minutes, the free iodine is removed by adding thiosulphate and the iodo-antipyrine extracted by shaking thrice with 25 c.c. of chloroform each time. The chloroform extract is washed with water, filtered, evaporated and the residue dried during 30 minutes at 110° and weighed. The weight multiplied by 0.5992 gives the quantity of antipyrine.

II. *When antipyrine is mixed with acetanilide, phenacetin, sulphonal or other substances which do not give an iodine-derivative insoluble in aqueous acid.*

The sample (containing not more than 0.25 gm. of antipyrine) is dissolved in 50 c.c. of water and shaken well with 20 c.c. of concentrated hydrochloric acid and 50–60 c.c. of *N*/10 iodine; after 3 hours, the clear liquid is decanted through a filter of glass wool and asbestos and the tarry precipitate of antipyrine periodide washed eight to nine times by decantation with 5% hydrochloric acid, and dissolved in 50 c.c. of methyl alcohol free from ethyl alcohol and acetone. The solution is treated with 5 c.c. of sodium hydrogen carbonate solution and 50 c.c. of water, shaken for 5 minutes, whereby the periodide is converted into iodo-antipyrine, the excess of iodine is removed by thiosulphate and the iodo-antipyrine extracted by shaking three times with 40 c.c. of chloroform each time and estimated as described in I.

### Qualitative Tests for Antipyrine and Pyramidone.

According to Javillier<sup>3</sup> in a solution of antipyrine containing 0.7% of hydrochloric acid, silicotungstic acid produces a *white* precipitate of the

<sup>1</sup> *Zeit. anorgan. Chem.*, 1913, 83, 119.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1914, 6, 1751.

<sup>3</sup> *Bull. Sci. Pharmacol.*, 1912, 19, 70.

composition  $\text{SiO}_2$ ,  $12\text{WO}_3$ ,  $2\text{H}_2\text{O}$ ,  $4\text{C}_{11}\text{H}_{12}\text{ON}_2$ ,  $7\text{H}_2\text{O}$ , which loses  $3\frac{1}{2}\text{H}_2\text{O}$  at  $120^\circ$ . A visible precipitate is produced in a solution containing only 1 part of antipyrine in 10,000. Under similar conditions in solutions of pyramidone containing 0.35% of hydrochloric acid, a *yellow* amorphous precipitate,  $\text{SiO}_2$ ,  $12\text{WO}_3$ ,  $2\text{H}_2\text{O}$ ,  $3\text{C}_{12}\text{H}_{17}\text{ON}_2$ ,  $8\text{H}_2\text{O}$  is produced which loses the whole of its water at  $120^\circ$ .

According to Moulin<sup>1</sup> pyramidone produces a blue colouration with solutions of silver or mercury nitrate. No colouration is produced with pure nitric acid but if the acid contains nitrous acid, the colouration is obtained.

#### ERRATA IN VOL. VI.

Page 1, line 5 from bottom, "triamin-compounds," should read "triamino-compounds."

Page 4, line 2, "calcium hydroxide" should be "calcium oxide."

Page 36, first line of footnote, "levulinic" should be "lævulinic."

Page 49, line 2 from bottom, "halagen" should read "halogen."

<sup>1</sup> *Ann. Chim. Analyt.*, 1912, 17, 13.



# ANILINE AND ITS ALLIES.

By S. S. SADTLER.

## ESTIMATION OF ACETANILIDE AND PHENACETIN IN ADMIXTURE.

**Phenacetin.**—W. O. Emery<sup>1</sup> gives the following procedure: Into a small (50 c.c.) lipped Erlenmeyer flask introduce 0.2 gm. of the phenacetin-acetanilide mixture, add 2 c.c. of glacial acetic acid, heat gently over wire gauze to complete solution, then dilute with 40 c.c. of water previously warmed to 70°. Transfer the clear acetous liquid, by pouring and careful washing of the flask with two 10 c.c. portions of warm (40°) water, into a glass-stoppered, graduated 100 c.c. flask, into which have been previously run from a burette 25 c.c. of standard iodine, of a strength slightly above  $N/5$  and warmed to 40°. Rotate the resulting menstruum to uniformity, the flask being closed meanwhile, then add 3 c.c. of concentrated hydrochloric acid, close flask again and continue rotation until copious crystallisation is apparent, then set the product aside to cool. If the ratio of phenacetin to acetanilide is equal to or greater than 1, crystalline scales will form almost immediately on adding the acid. As the proportion of acetanilide increases, however, the periodide is not only more inclined to maintain the liquid state, with the result that crystallisation becomes proportionately slower, but its separation also from the menstruum itself is in a measure retarded. In such cases, gentle agitation of the liquid or rotation of the flask in water warmed to 40° or less tends to promote the formation of crystals. When the contents of the flask have assumed the temperature of the room, fill up with water to within 2 to 3 c.c. of the mark, rotate to uniformity and allow to stand over night. Fill to the mark with water, mix thoroughly, then after standing 30 minutes withdraw a 50 c.c. aliquot of clear liquid by passing through a small (5.5 cm.) dry, closely fitted filter into a graduated 50 c.c. flask; the first 15 c.c. of the first runnings should be rejected, being received in any convenient container for eventual use later, along with additional filtrate, for the recovery of acetanilide. Transfer the 50 c.c. aliquot by pouring and washing to a 200 c.c. Erlenmeyer and titrate with  $N/10$  sodium thiosulphate.

If the composition is considered of the insoluble addition product,  $(C_2H_5O.C_6H_4NH.COCH_3)_2.HI.I_4$  formed in the foregoing separation, it will be noted that, for every molecule of phenacetin involved, 2 atoms of iodine are required; hence from a titrimetric standpoint, 1 atom of iodine is equivalent to  $\frac{1}{2}$  mol. of phenacetin. If, therefore, the quantity

<sup>1</sup> *J. Ind. Eng. Chem.*, 1914, 6, 665.

of iodine expended in the formation of insoluble periodide is ascertained as the result of such titration, the quantity of phenacetin thereby involved is readily calculated from the expression,

$$\text{phenacetin} = I (0.008890 \times N)$$

in which 0.008890 represents the quantity of phenacetin in 1 c.c. of an  $N/10$  solution of this substance,  $N$  the normality of standard thiosulphate employed, while  $I$  represents the number of c.c. of such combination with phenacetin isolated as periodide.

The gravimetric estimation of phenacetin may, if desired, be effected substantially as follows: In the operation of filtering off the periodide, the latter is collected on the filter and washed with 10 to 15 c.c. of standard iodine solution, preferably by suction, then transferred, together with the filter (likewise any particles of precipitate which may remain in the graduated flask) to a separating funnel, using for the purpose not more than 50 c.c. of water. After discharging both free and added iodine with a few small crystals of sodium sulphite, the liquid is extracted with three 50 c.c. portions of chloroform, each portion being subsequently washed in a second separating funnel with 5 c.c. of water. After washing and clearing, the solvent is passed through a small (5.5 cm.) dry filter into a 200 c.c. Erlenmeyer, most of the chloroform removed by distillation, and the residual 5 to 10 c.c. are transferred by pouring and washing with fresh solvent into a small tared beaker or crystallising dish. The solution is evaporated to dryness on the steam-bath, and the residue cooled and weighed.

**Acetanilide.**—Should the combined weight of the phenacetin-acetanilide mixture be known, that of the latter constituent can be determined by difference, or, if necessary, estimated directly from a second aliquot of filtrate from the phenacetin-periodide.

To this end, transfer to a separating funnel by means of a pipette 25 to 30 c.c. of the clear liquid, decolourise with sufficient solid sodium sulphite, add solid hydrogen sodium carbonate in slight excess, follow with 1 to 2 drops of acetic anhydride, then extract with three 60 c.c. portions of chloroform, passing the solvent when cleared through a small, dry filter into a 200 c.c. Erlenmeyer flask; the chloroform is distilled off by the aid of gentle heat until the volume is about 20 c.c. Now add 10 c.c. of dilute sulphuric acid (1 c.c. of concentrated acid to 10 c.c. of water) and digest the product on the steam-bath until the aqueous residue has been reduced to one-half, add 20 c.c. of water and continue the digestion 1 hour, add a second 20 c.c. portion of water and 10 c.c. of concentrated hydrochloric acid, then titrate very slowly drop by drop, with standard potassium bromide-bromate (1 c.c. of which is equivalent to 5 to 10 mg. of acetanilide), until a faint yellow colouration persists. While adding this reagent, the flask should be rotated sufficiently to agglomerate the precipitated tribromaniline and thus clarify the supernatant liquid. The number of c.c. of standard bromide solution required

to complete the precipitation, multiplied by the value of 1 c.c. in terms of acetanilide, will give the quantity of this substance present in the aliquot taken.

### ERRATA IN VOL. VI.

Page 57, line 3 from bottom, for "sulphate" read "sulphide." Line 2 from bottom, for "as" read "at."

Page 58, line 12, for "if" read "it."

Page 59, line 11 from bottom, for "hydrochlorate" read "hydrochloride."

Page 60, line 18 from bottom, for "or pure aniline hydrochlorate" read "of pure aniline hydrochloride."

Page 60, line 3 from bottom, for "centimetres" read "cubic centimetres."

Page 63, line 5 from bottom, formula for toluidines should be  $C_7H_7.NH_2$  not  $C_7H_7.HN_2$ .

Page 66. The top paragraph, from "*p*-Toluidine is produced" to "recalling that of aniline" should be transferred to page 65, and inserted after the paragraph dealing with meta-toluidine."

Page 68, line 16, for "phosphates" read "phosphoric acid." Line 23 for "hydrochlorates" read "hydrochlorides."

Page 69, line 1, for "the" read "then."

Page 71, footnote line 4, for "o-oxylidine" read "o-o-xylylidine."

Page 75, line 8 from bottom, for "hydrochlorate" read "hydrochloride."

Page 76, line 1 for "which" read "while."

Page 82, line 12 from bottom, for "Acet-phenethidine" read "acet-phenetidine."

Page 85, footnote, for "amido" read "amino," and for "levorotatory" read "laevorotatory."

Page 86, line 12, for "phenylformamid" read "phenylformamide."

Page 86, line 16, for "anesthetic" read "anæsthetic." Line 17, for "Gallanid" read "Gallanide."

Page 89, in footnote delete lines 2 to 4, which duplicate the text.

Page 90, line 13 from bottom, for "Vol. 4" read "Vol. 5."

Page 92, line 4 below table for "methylaniline" read "methylaniline."

Page 93, line 1 for "acetylisation" read "acetylation." Line 6, delete "Recognition of in the presence." Line 7, after bracket add "as follows." Line 10 and line 13, for "Cl" read "Cl." Second line from bottom, for "aliquod" read "aliquot."

Page 96, line 3; delete the whole of this line. Line 17, for equation given, read  $(C_6H_5)_2NH + 8Br = (C_6H_5Br)_2NH + 4HBr$ .

Page 97, line 3, delete "J. W. G."

Page 97, line 2 from bottom for "*p*-minophenol" read "*p*-aminophenol."

Page 98, line 12 for "anisols" read "anisoles." Line 13, for "phenethidine" read "phenetidine." Line 13, for "aminophenatols" read "aminophenetoles." Line 15 for "Anisol" read "Anisole;" "Phenatol" read "Phenetole." Line 17, for "metacetin" read "methacetin." In table, division 4 from bottom, for "phenethidine" read "phenetidine."

Page 99, line 13 and line 19 for "acetphenetidin" read "acetphenetidine."

Page 100, line 15 and line 9 from bottom, for "phenetidin" read "phenetidine." Line 6 from bottom for "diaminophenatols" read "diaminophenetoles."

Page 102, line 3 for "Million's" read "Millon's."

Page 104, line 21 from bottom, for "phenethidine" read "phenetidine." Line 16 from bottom, for "phenetidin" read "phenetidine." Line 12 from bottom, for "amidin" read "amidine." Line 9 from bottom, for "anesthetic" read "anæsthetic."

Page 107, line 14 for "Diamiotoluenes" read "Diaminotoluenes."

Page 109, line 18 from bottom, for "Orthotoluidine" read "Orthotolidine." Line 5 from bottom, for "Toluidine" read "Tolidine."

# THE NAPHTYLAMINES AND THEIR ALLIES.

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By EDWARD HORTON.

## PYRIDINE.

**Detection.**—To detect pyridine in "Liquor Ammonii caustici" Kunze-Krause<sup>1</sup> recommends that 11 or 12 c.c. of the liquor contained in a test-tube should be neutralised gradually, but as quickly as possible, by adding 5 grm. of powdered tartaric or citric acid, the mixture being constantly stirred. Before and after the addition of the final quantity of acid, the hot liquid is thoroughly shaken and immediately smelt. When the smell of ammonia has disappeared, it should be odourless. Very small quantities of pyridine give a recognisable smell.

Wöhlk<sup>2</sup> detects pyridine in ammonium salts by grinding about 0.5 grm. of the latter in a mortar with 1 grm. of borax. If pyridine be present it is immediately recognised by its characteristic odour.

**Estimation.**—In the analysis of mixtures of ammonia and pyridine, Delépine and Sornet<sup>3</sup> remove the ammonia by Gerresheim's method,<sup>4</sup> by precipitating it from solution in hydrochloric acid with mercuric chloride in the presence of sodium carbonate and sodium hydroxide. The pyridine is distilled out of the filtrate and weighed either as the aurichloride or the platinichloride.

Bayer<sup>5</sup> states that in titrating pyridine in ammonium salts, ferric thiocyanate is a more satisfactory indicator than either methyl orange or ferric chloride. The mixed bases are acidified with *N*/10 hydrochloric acid, treated with a drop of ferric chloride solution, and one of ammonium thiocyanate solution and titrated with *N*/10 sodium hydroxide solution until the brownish-red colour is destroyed. The bases can be partially separated by distilling the neutral solution of the mixed salts, when the pyridine passes over together with a very small amount of ammonia. The latter is titrated with *N*/10 hydrochloric acid in the presence of litmus, then excess of acid is added and the pyridine estimated as above.

A method of estimating pyridine in ammonia water, which depends on

<sup>1</sup> *Apoth. Zeit.*, 1910, 25, 87.

<sup>2</sup> *Ber. deut. Pharm. Ges.*, 1912, 22, 825.

<sup>3</sup> *Bull. Soc. Chim.*, 1911 [iv], 9, 706.

<sup>4</sup> *Annalen*, 1879, 195, 373.

<sup>5</sup> *J. Gasbel.*, 1912, 55, 513.

the destruction of the ammonia with sodium hypobromite has been described by Houghton.<sup>1</sup> 100 c.c. of the ammonia water are diluted with 150 c.c. of distilled water in a litre flask and a few drops of methyl orange solution added. The flask is cooled in running water and the liquid neutralised with dilute sulphuric acid (1:3) and made slightly acid, then 5 c.c. of *N*/1 NaOH solution are added and the liquid distilled (if the proportion of pyridine present is high, either a smaller volume of ammonia water must be used or more than 5 c.c. of *N*/1 alkali solution added). To destroy the ammonia, the distillate is treated with 100 c.c. of a sodium hypobromite solution (prepared by dissolving 100 gm. of sodium hydroxide in a litre of water and adding 25 gm. of bromine) and shaken until no more gas is evolved. The unchanged pyridine is then distilled into excess of *N*/10 acid, the excess being titrated with *N*/10 alkali using methyl-orange as indicator (1 c.c. *N*/10 acid is equivalent to 0.0079 gm. pyridine). A more rapid modification of the same method is described by Baessler,<sup>2</sup> in which the vapour from the slightly alkaline solution of ammonium and pyridine sulphates is made to pass through a sodium hypobromite solution, the vapour from which (containing pyridine only) is collected in the *N*/10 acid.

It is stated by Fincke<sup>3</sup> that a proportion of the spirit used in the manufacture of vinegar has been denatured with pyridine, which accordingly occurs in the resulting product. For its estimation therein Fincke holds that Lunge's method (*Chem. Techn. Unters. Methoden*, 5th Ed., Berlin, 1905, 3, 583) is inaccurate, and recommends that described by Houghton (*loc. cit.*).

### Pyrrole.

Herzfeld describes<sup>4</sup> the following simple test for pyrrole, which has the advantage of distinguishing it from indole. An indole solution when treated with solutions of sodium hydroxide and sodium nitroprusside acquires a violet blue colour, which on addition of acetic acid becomes blue. Under the same conditions a pyrrole solution gives a brownish-red colour, which, unlike the violet blue of indole, can be extracted with chloroform. With a solution containing both indole and pyrrole after shaking with chloroform, a liquid is obtained which consists of a blue upper layer and a brownish-red lower layer.

### ERRATUM IN VOL. VI.

Page 121, headline, for "sulphuric acids" read "sulphonic acids."

<sup>1</sup> *J. Ind. Eng. Chem.*, 1909, 1, 698.

<sup>2</sup> *J. Gasbel.*, 1912, 55, 905.

<sup>3</sup> *Zeitschr. Nahr. Genussm.*, 1911, 21, 655.

<sup>4</sup> *Biochem. Zeit.*, 1913, 56, 82.

# THE VEGETABLE ALKALOIDS.

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By THOMAS A. HENRY, D. Sc.

Since the date of the previous article a great deal of work on alkaloids has been published but it is mainly concerned either with the determination of the constitution of well-known alkaloids, or with the isolation and characterisation of new alkaloids. Comparatively few new facts which affect alkaloids as a class have been recorded.

**Formation and Function of Alkaloids in Plants.**—In the original article it was pointed out that two views are held as to the mode of formation of alkaloids in plants. Some authorities believe that they are products of direct synthesis, whilst others regard them as formed, directly or indirectly by the decomposition of proteins first formed. It seems to be clearly established that where alkaloids do not occur in the seeds of plants, which normally contain them, they are produced almost as soon as the seeds germinate: thus Torquati<sup>1</sup> found that ungerminated barley is free from hordenine but that the base is formed immediately on germination and steadily increases in amount until the fourth day when it reaches a maximum and then gradually diminishes. Similarly Kerbosch<sup>2</sup> found that although the seed of the opium-poppy contains only a trace of narcotine and amorphous alkaloids, the amount of narcotine increases on germination and the other characteristic opium alkaloids appear in the order, codeine, morphine, papaverine, narceine, and thebaine. This increase occurs even when the seeds are germinated in a nitrogen-free atmosphere, whence it appears that the narcotine and other alkaloids are formed at the expense of protein. de Plato's observation that tobacco seed is free from cyanogenetic glucosides and alkaloids but contains allantoin is also of interest in this connection.<sup>3</sup> Ciamician and Ravenna have applied their inoculation method to tobacco<sup>4</sup> and find that whilst inoculation with asparagine or dextrose causes an increased production of alkaloids, the application of pyridine, piperidine, or pyrrolecarboxylic acid does not, in spite of the fact that nicotine, the chief tobacco alkaloid is *N*-methyl- $\alpha$ - $\beta$ -pyridylpyrrolidine. The results of all this work still leave the question of the mode of formation of alkaloids open, though on the whole they may be said to lend support to the view that alkaloids are formed from the decomposition products of proteins or at least from similar amino-compounds.

<sup>1</sup> *Arch. Pharmacol. experim.*, 1910, 10, 62 and 97.

<sup>2</sup> *Pharm. Weekblad*, 1910, 47, 1062, 1081, 1106.

<sup>3</sup> *Stas. sper. Agrar. ital.*, 1910, 43, 79.

<sup>4</sup> *Atti. R. Accad. Lincei*, 1911 [v], 20, i, 614.



Closely allied to this subject is that of the function of alkaloids in plants. Probably no one now seriously holds the view that alkaloids are a means of protection for the plants which produce them. The view most widely accepted is that they are ultimate products of metabolism and of no further use to the plant. Apart from the facts supporting this view referred to in the original article, van Leersum<sup>1</sup> has disproved Lotsy's contention that in cinchona amorphous alkaloids are produced in the leaves under the stimulus of light and air, and are then transported to the stem where they are elaborated into quinine and cinchonine. According to van Leersum the two latter alkaloids are formed in the leaves and the amount in these members remains constant even after the leaves have fallen from the tree. Tunmann<sup>2</sup> has investigated the behaviour of the alkaloids in nux vomica seeds and shown that there is no ground for the view that in this case the alkaloids are used by the embryonic plant.

The most useful evidence recently brought forward for the opposite view, viz., that alkaloids are assimilation products destined to serve the purposes of nutrition in the plant is that produced by Schmidt<sup>3</sup> and his collaborators, Müller<sup>4</sup> and Klee.<sup>5</sup> Müller in particular has shown that in the opium-poppy grown under natural conditions, alkaloids begin to appear in the plant 14 days after germination; the amount increases until reserve albumin begins to accumulate in the seeds, when it begins to diminish in the leaves, fruits and stems though it never disappears entirely from these organs, whence Müller concludes that in this species at least, the alkaloids are used in producing protein during the ripening of the seed. A certain amount of support for this view is also afforded by Schloesing's observation<sup>6</sup> that a normally grown tobacco plant contains much less nicotine than one from which the leaves have been partially removed.

**Properties of the Alkaloids.**—It was pointed out in the original article that most alkaloids are optically active and that certain alkaloids (e.g., nicotine and aconitine) exhibit a rotatory power opposite in sign to that of their salts. Carr and Reynolds have shown<sup>7</sup> that though comparatively few alkaloids show a change in the sign of the rotatory power on neutralisation, a change in the value of the rotatory power is not uncommon especially among the tertiary alkaloids, even when both determinations are made in the same dissociating solvent; thus *L*-hyoscyne in water has  $[\alpha]_D - 28.0^\circ$  as base and  $[\alpha]_D - 32.8^\circ$  in the form of a salt. Quinine in 50% alcohol has  $[\alpha]_D - 170.5^\circ$  as base and  $[\alpha]_D - 262.1^\circ$  as salt. It is well known that the nature of the solvent and the concentration of the solution also affect the rotatory power of certain alkaloids and the same authors record new instances of the effect of these factors; thus hydrastine in the form of hydrochloride has  $[\alpha]_D + 158^\circ$

<sup>1</sup> *Proc. K. Akad. Wetensch., Amsterdam*, 1910, 13, 210.

<sup>2</sup> *Arch. Pharm.*, 1910, 248, 644.

<sup>3</sup> *Ber. deut. pharm. Ges.*, 1914, 24, 35.

<sup>4</sup> *Arch. Pharm.*, 1914, 252, 280.

<sup>5</sup> *Ibid.*, 211.

<sup>6</sup> *Compt. rend.*, 1910, 151, 23.

<sup>7</sup> *Trans. Chem. Soc.*, 1910, 97, 1328.



in water, and  $+197^{\circ}$  in 50% alcohol. The same alkaloid, as free base, is strongly dextrorotatory in 50% alcohol, optically inactive in 95% alcohol and markedly laevorotatory in 100% alcohol.

**General Precipitants for Alkaloids.**—A certain number of new precipitants for alkaloids have been described but none of these appears at present to offer any advantages over those already in common use.

Silicotungstic acid, first used by R. Godeffroy as a precipitant for alkaloids in slightly acid solution has acquired some importance recently owing to its having been applied to the estimation of nicotine, atropine, and other alkaloids, especially by Bertrand and Javillier.<sup>1</sup>

#### ERRATA IN VOL. VI.

Page 167, line 5 from bottom, insert after the bracket "are small in number" and delete the next nine words.

Page 168, line 7, replace "No alkaloid has" by "Only two alkaloids have."

Page 172, line 11 after "weight of" insert "magnesia or."

Page 172, line 4 from bottom, for "South Wark" read "Southwark."

Page 173, line 3 from bottom, between "the" and "ground" insert "dry."

Page 174, line 15 from bottom, after "residue" delete "extracted" and insert "thoroughly mixed."

Page 177, line 17 from bottom; delete this and two next lines.

Page 181, line 12 from bottom, after "phenolphthalein" insert (cf. Elvove, *J. Amer. Chem. Soc.*, 1910, 32, 132).

Page 182, bottom line, after "sparteine" insert "nicotine, pilocarpine."

Page 183, line 3 for "iodesin" read "iodeosin."

Page 184, line 2 from bottom, add at end "methods involving sublimation have been suggested recently for the detection or estimation of certain alkaloids. (Burmman, *Bull. Soc. chim.*, 1910 (iv), 7, 239; Eder, *Schweiz. Woch. Chem. Pharm.*, 1913, 51, 228, 241, 253; Tunmann, *Pharm. Zentr.-H.*, 1913, 54, 1065)."

Page 199, line 19, delete "and papaverine."

Page 201, line 7 from bottom, after "with" add "hydrogen peroxide."

Page 202, bottom line, for "produces" read "produce."

Page 203, line 7 from bottom, delete "and codeine."

Page 206, line 14 from bottom, delete all after "coca alkaloids."

<sup>1</sup> *Compt. rend.*, 1899, 128, 742; *Bull. Soc. chim.*, 1909 (iv), 5, 241; *Bull. Sci. Pharm.*, 1909, 16, 315; 1910, 17, 629; *U. S. Dept. Agric., Chem. Div. Bulletin No. 101*, of 1910; *Ann. Chim. Anal.*, 1911, 16, 251; *Gazette* 1913, 43, ii, 482 and *Schweiz. Woch. Chem. Pharm.*, 1913, 51, 761.

# VOLATILE ALKALOIDS.

By FRANK O. TAYLOR.

**Areca Alkaloids** (Compare Vol. VI, pp. 208-211).—**Arecolidine**.—H. Emde<sup>1</sup> has isolated from the mother liquors obtained in the preparation of arecoline hydrobromide minute quantities of a new alkaloid to which he gives the name *arecolidine* and assigns the formula  $C_8H_{13}O_2N$ , its constitution being probably  $CH:CH.C(OCH_3):C(OCH_3):CH_2.NCH_3$ . Separation is effected by the continued recrystallisation of the hydrochlorides. From the pure salt, arecolidine is liberated even by mild alkalis, such as magnesium carbonate. The base is easily soluble in water, alcohol, ether and acetone and on evaporation of the aqueous solution remains as a pleasantly odorous, thick oil. From anhydrous ether the base is obtained in brilliant needles, m.p.  $105^\circ$ , but sublimation raises this to  $110^\circ$ . The crystalline base is very hygroscopic. *Arecolidine hydrochloride*,  $(C_8H_{13}O_2N.HCl.H_2O)$  crystallises from 99.5% alcohol in hygroscopic prisms m.p.  $95^\circ-98^\circ$ . At  $100^\circ$  it loses its water and at  $250^\circ$  decomposes.

Tunmann<sup>2</sup> has found that the alkaloids are contained in the cells of the endosperm and not in the veiny tissue. He devised a method for the microscopical detection of the alkaloids in sections of the nuts, as follows:

Prepare a filtered solution of 0.1 gm. of picrolonic acid in a mixture of 3 c.c. alcohol and 2 c.c. water. Drop the prepared section into some of this solution on a slide, put on a cover glass, seal in place with wax and let stand. Within 2 days characteristic sphæro-crystals are formed inside the cellular tissue.

From the dry powder characteristic fatty acid crystals may be sublimed. In the original article both kinds of crystals are illustrated.

An acceptable method of assay is that of the Swiss Pharmacopœia, which requires a standard of 0.5% arecoline. To 12 gm. of powdered areca nuts contained in a tightly stoppered flask add 120 c.c. of ether and allow to macerate for 15 minutes with frequent shaking. Now add 5 c.c. of 10% ammonia and continue the digestion for an hour with frequent vigorous shaking, preferably continuously in an automatic shaker. Let stand until the supernatant ethereal solution is clear, and then decant 100 c.c. through a pledget of cotton into another flask, evaporate carefully to remove all ether, dissolve the residue in 5 c.c. of alcohol, add 10 c.c. of water, 3 drops of hæmatoxylin solution and 30 c.c. of ether, and titrate with *N*/10 hydrochloric acid till the

<sup>1</sup> *Apoth. Zeit.*, 1915, 30, 240.

<sup>2</sup> *Pharm. Post*, 1911, 44, 703.

colour of the aqueous layer begins to change; now add 30 c.c. of water and carefully finish the titration to a yellowish end-point, vigorously shaking. During this treatment at least 3.3 c.c. of *N*/10 acid should be consumed, equal to not less than 0.5% arecoline in the drug. The same process may be applied to fluid and solid extracts by evaporating equivalent amounts to dryness on washed sawdust, taking this in place of the powdered drug.

By this process Puckner<sup>1</sup> found 0.44% and 0.52% in two samples.

**Conium Alkaloids** (Vol. VI, pp. 211-223).—Since the publication of Vol. VI there has been no work on these alkaloids having any important bearing on analytical processes.

Neogi<sup>2</sup> in the course of work on nitrites of various bases produced *coniinium nitrite* by repeated distillation *in vacuo* of a mixture of coniine hydrochloride and an alkali nitrite. This substance forms deliquescent, fibrous crystals which melt at 84° and sublime *in vacuo*. When heated to 120° under atmospheric pressure it forms *nitrosoconiine*. He also obtained *coniine methonitrite*,  $C_8H_{17}N \cdot CH_3 \cdot NO_2$ , as a viscous reddish-yellow liquid.

A method for the assay of conium that in several ways is preferable to others described in Vol. VI is one worked out in Parke, Davis & Co.'s laboratory.

To 10 gm. of the finely powdered drug add 5 c.c. of 5% hydrochloric acid and 50 c.c. of petroleum ether (ligroin); shake well for 5 minutes and let settle. Decant the petroleum ether and repeat the operation. After the second washing (which operation removes the fat that otherwise interferes with the assay) remove the petroleum ether fully by decantation and evaporation of the last portions in a current of air. Now add to the still moist drug, in a tightly stoppered flask, 80 c.c. of petroleum ether and 1 gm. of potassium carbonate; shake well for several minutes and let stand over night. Transfer exactly 40 c.c., representing 5 gm. of the drug, through a pledget of cotton to another flask, add 10 c.c. of *N*/10 acid, evaporate the petroleum ether at a low temperature, preferably under a current of warm air, and titrate the excess acid with *N*/50 alkali. Each c.c. of *N*/10 acid consumed equals 0.0127 gm. coniine.

The fluid extract may be treated directly by the same process without previously evaporating it.

**Lobeline** (Vol. VI, pp. 223-225).—Owing to its comparatively restricted use, lobelia and its alkaloids have received practically no attention during the last 3 years.

**Lupine Alkaloids** (Vol. VI, pp. 225-229).—The high protein content of the lupines makes them especially useful as fodder for animals were it not for the marked bitter taste due to the alkaloids. This bitterness may be removed by washing with water and drying, or preferably by steaming, after which the plants are mashed between hot rollers to produce the so-called

<sup>1</sup> *Rep. Lab. Am. Med. Assoc.*, 4, 119.

<sup>2</sup> *Trans.*, 1912, 101, 1608.

"lupine flakes." Assays of these by Stutzer and Gay<sup>1</sup> gave the following results:

Crude protein.....	37.06 %	31.93 %
Crude fat.....	4.20 %	3.89 %
Nitrogen free extractive.....	41.48 %	39.10 %
Crude fibre.....	13.46 %	7.02 %
Digestible protein.....	31.55 %	

See also Honcamp.<sup>2</sup>

**Dextro-lupanine** (VI, p. 228) has been compared with oxysparteine, by Beckel,<sup>3</sup> who finds that these alkaloids are not identical since they give different halogen alkyl derivatives. He also<sup>4</sup> fails to verify the work of Soldaini and of Davis who obtained two new bases having the formulæ  $C_8H_{15}ON$  and  $C_7H_{11}O_2N$ , by the action of bromine on *d*-lupanine hydrochloride in alcoholic or acetic solution. By similar treatment Beckel claims the formation of *ethoxylupanine dihydrobromide*,  $C_{15}H_{25}ON_2 \cdot OC_2H_5 \cdot 2HBr$ , which forms colourless needles from hot alcohol, m. p. 227–228°, very soluble in water but difficultly so in alcohol,  $[\alpha]_D = -129.4^\circ$  in 0.8% to 3.1% aqueous solution, or in 1.7% alcohol. Ethoxylupanine also forms a *dihydroiodide* on boiling the dihydrobromide with hydriodic acid; it forms needles from alcohol, m. p. 221–222°,  $[\alpha]_D = -106.2^\circ$  (0.2627 grm. in water to make 19.66 c.c.). A *thiocyanate* has been described, crystallising in needles, easily soluble in water and slightly soluble in alcohol, m. p. 172–174° and  $[\alpha]_D = -133.4^\circ$  (0.3983 grm. in water to 18.66 c.c.).

*d*-Lupanine dihydrobromide,  $C_{15}H_{24}ON_2 \cdot 2HBr \cdot H_2O$ , forms needles, m. p. 188°–189°,  $[\alpha]_D = +45.9^\circ$ , which on drying lose both water and hydrogen bromide.

Di Palma<sup>5</sup> describes the action of heat up to 300° on *d*-lupanine, stating that after the evolution of alkaline gases smelling of pyridine there can be isolated from the residue a base having the formula  $C_{15}H_{22}N_2$  which gives a *hydrochloride* melting with decomposition at 165°; a *platinichloride* + 5H<sub>2</sub>O, m. p. (when dried) 117°–119°, and an *aurichloride* melting with decomposition at 160°–165°.

*Inactive lupanine* was found by Beckel (*loc. cit.*) in the seeds of *Lupinus angustifolius*, as the chief constituent of alkaloids present to the extent of 0.9% to 1.2% and in the pods about one-fifth as much. A crude alkaloid from the seed prepared by extraction with alcoholic hydrochloric acid consisted of about 38% of *hydroxylupanine*, which may possibly have been formed during the extraction process. He describes an abnormal aurichloride and platinichloride of the *dl*-lupanine methochloride.

**Piturine.**—The work of Rothera<sup>6</sup> has verified and supplemented that of Langley and Dickinson and of Petit, with the result that piturine is found to be identical with nicotine, and not a distinct alkaloid.

<sup>1</sup> Landw. Vers. Sta., 1913, 78–80, 219; Chem. Abst., 1913, 7, 2811.

<sup>2</sup> Wiener. Landw. Zig., 63, 315.

<sup>3</sup> Arch. Pharm., 1911, 249, 329.

<sup>4</sup> Ibid., 250, 691.

<sup>5</sup> Giorn. Farm. Chim., 1913, 61, 151.

<sup>6</sup> Bio-chem. J., 1910, 5, 193.

**Pomegranate Alkaloids.**—No new information of analytical interest has appeared since the publication of Vol. VI.

**Sparteine and other Spartium Alkaloids** (Vol. VI, pp. 232–235).—During the past few years considerable work has been done in attempts to elucidate the exact constitution of sparteine, but not much of it is of analytical interest. For theoretical considerations and a mass of data sustaining them see Moureu and Valeur;<sup>1</sup> Germain,<sup>2</sup> and Corriez.<sup>3</sup>

Corriez describes the following new salts of sparteine:<sup>4</sup>

*Dichlorate*,  $C_{15}H_{28}N_2 \cdot 2HClO_3$ , decomposing explosively at  $147^\circ$  without melting;  $[\alpha]_D = -23.12^\circ$ .

*Monochlorate*,  $C_{15}H_{28}N_2 \cdot HClO_3$ , m. p.  $139^\circ$ – $140^\circ$ , exploding at  $200^\circ$ – $205^\circ$ ;  $[\alpha]_D = -16.3^\circ$ .

*Diperchlorate*,  $C_{15}H_{28}N_2 \cdot 2HClO_4 \cdot 2H_2O$ , m. p.  $78^\circ$ , but if anhydrous at about  $265^\circ$ , exploding at  $300^\circ$ ,  $[\alpha]_D = -17.3^\circ$ .

*Monoperchlorate*,  $C_{15}H_{28}N_2 \cdot HClO_4$ , m. p.  $171^\circ$ , decomposing at  $300^\circ$ ;  $[\alpha]_D = -16.3^\circ$ .

*Dichromate*,  $C_{15}H_{28}N_2 \cdot H_2Cr_2O_7$ , darkens in the light and decomposes on heating, soluble in 50 parts of water.

*Salicylate*,  $C_{15}H_{28}N_2 \cdot 2C_7H_6O_3 \cdot H_2O$ , m. p.  $78^\circ$ ;  $[\alpha]_D = -9.42$ .

He also describes<sup>5</sup> the *perbromide* made by the action of bromine in fuming hydrobromic acid on sparteine dissolved in the same acid; this interaction may be used to detect sparteine. By adding 2 c.c. of the aqueous solution to be tested to an equal volume of hydrobromic acid containing a small quantity of free bromine (1 or 2%), the presence of as little as 0.01 mg. of sparteine will show a yellowish precipitate. (The perbromide melts at  $193^\circ$ ).

In an attempt to produce habituation to sparteine, Dolencourt<sup>6</sup> demonstrated by intramuscular injections that the lethal dose of sparteine sulphate in guinea-pigs is 0.0066 grm. per 100 grm. of body weight, which, if the same held true for human beings would be the extraordinary amount of 4.5 grm. (about 70 grains) per 150 pounds.

*Genisteine*,  $C_{16}H_{28}N_2$ , is a new volatile, crystalline base of low melting point discovered by Valeur<sup>7</sup> in the mother liquors from the crystallisation of sparteine sulphate. It melts at  $60.5^\circ$  and boils at  $177^\circ$ – $178^\circ$  (not corr.). Potassium permanganate in sulphuric acid does not oxidise it. The following salts are described:

*Hydrate*,  $C_{16}H_{28}N_2 \cdot H_2O$ , m. p.  $117^\circ$ ;  $[\alpha]_D$  (4% solution in alcohol) =  $-52.34^\circ$ . *Picrate*, m. p.  $215^\circ$  (with decomposition). *Platinichloride*,

<sup>1</sup> *Comp. rend.*, 1912, 154, 161 and 309; and chiefly *Ann. Chim. phys.*, 1912, 27, 245–391 which is a résumé of some 10 years' work previously published in various journals.

<sup>2</sup> *Gazzetta*, 1912, 42, i, 447.

<sup>3</sup> *Bull. sci. pharmacol.*, 1912, 19, 468, 527, 533, 620.

<sup>4</sup> *Ibid.*, 19, 468.

<sup>5</sup> *Ibid.*, 19, 533.

<sup>6</sup> *Compt. rend. soc. biol.*, 1913, 74, 801.

<sup>7</sup> *J. pharm. chim.*, 1913, 8, 573.

crystallising with  $2\text{H}_2\text{O}$  which it loses at  $110^\circ$ ; blackens without melting at  $235^\circ$ .

#### ERRATA IN VOL. VI.

Page 207, line 13, for "Lupinined" read "Lupinidine."

Page 210, line 30, for "Jahrs" read "Jahns."

Page 211, lines 3 and 21, for "*Jahr's*" read "Jahns."

Page 212, in table, for "methyl-conine" read "methyl-coniine."

Pages 213, 215, 217, 219, 221 title, for "ARECA OR BETEL-NUT" read "CONIUM OR HEMLOCK."

Page 233, line 17, for "sparteine" read "sparteine sulphate."

# ESTIMATION OF NICOTINE.

By R. W. TONKIN.

The frequency with which the estimation of nicotine is hindered by the presence of ammonia or substances which yield it on treatment with alkalies has led to the introduction of polarimetric methods.

Tóth<sup>1</sup> modifies his method, given in Vol. VI of this work (page 240) by substituting xylene for the extracting agent and calculates the amount of nicotine by observing the rotation of the fluid, the specific rotation of nicotine in a dilute xylene solution being  $+173^{\circ}$ .

König<sup>2</sup> in the case of tobacco extracts, dilutes 10 c.c. with 5 c.c. of water, adds 2 c.c. of 1:1 sodium hydroxide solution and some glass beads, and extracts the nicotine by shaking for 2 hours with 50 c.c. of toluene. Xylene can be substituted for toluene. The nicotine is calculated from the observed rotation. The nicotine can then be titrated by shaking with water and standard acid using iodeosin as indicator as usual.

Bertrand and Javillier<sup>3</sup> heat 12 grm. of tobacco in a flask with reflux condenser for an hour with 300 c.c. of 0.5% hydrochloric acid; after cooling, the contents of the flask are filtered, and 250 c.c. of the filtrate are treated with a 10–20% solution of potassium silico-tungstate in slight excess. If nicotine is present in any quantity, a precipitate forms rapidly, but it is advisable to let the mixture stand for a day or two to ensure that the whole is precipitated. The composition of the precipitate dried at  $130^{\circ}$  is expressed by the formula.  $[12\text{WO}_3, \text{SiO}_2, 2\text{H}_2\text{O} : 2\text{C}_{10}\text{H}_{14}\text{N}_2]$ . The composition is not quite constant when thus dried, but the nicotine may be calculated from the weight of the residue left on ignition by using the factor 0.1071.

As many other bodies give a similar precipitate with the silico-tungstate solution, it is preferable to distil off the nicotine and titrate it in the distillate. The precipitate is introduced in a flask with 125 c.c. of water and some magnesium oxide and 100 c.c. distilled over, when the whole of the nicotine will have been expelled.

The method is a good one for estimating small amounts of nicotine when time is no object.

Harrison and Self<sup>4</sup> give the following: An amount of tobacco or extract is taken which will yield about 0.5 grm. nicotine, mixed with lime and water

<sup>1</sup> *Chem. Zeit.*, 1911, 35, 926.

<sup>2</sup> *Chem. Zeit.*, 1911, 35, 521.

<sup>3</sup> *Bull. Soc. Chim.*, 1909 [iv], 5, 241.

<sup>4</sup> *Pharm. J.*, 1912, 34, 718.



and steam-distilled till the whole of the volatile bases have passed over; these are absorbed in a measured amount of standard acid and the total bases determined by titrating back. 10 c.c. of the acid are then added and the liquid evaporated to 50 c.c. (no ammonia is lost by this process) and iodine dissolved in potassium iodide solution is added to precipitate the nicotine. The iodine should be 10 times that required to combine with the total bases calculated as nicotine. The solution is made up to 100 c.c. and filtered; 75 c.c. of the filtrate are taken and the excess of iodine removed with sodium thiosulphate. After adding 25 c.c. of 10% sodium hydroxide solution, the ammonia is distilled off into an excess of standard acid, and determined by titrating back. The difference between the total bases and the ammonia is returned as nicotine.

A large excess of alkali is necessary in the last distillation as otherwise the liquid may become acid, probably owing to the decomposition of the tetrathionate formed while removing the excess of iodine.

R. Spallino<sup>1</sup> publishes a method based on the fact that nicotine in alcoholic solution acts as a mono-acidic base towards picric acid, whereas in aqueous solution it is diacidic.

The liquid containing nicotine is treated with an excess of picric acid solution of known strength (9 mg. per c.c.), and the mixture made up to 1 litre with alcohol; it is then divided into 2 equal parts which are evaporated to dryness. In one case the residue is dissolved in alcohol and titrated with *N*/20 barium hydroxide. The other portion is rubbed up with water, made up to 100 c.c. filtered to remove undissolved picrate, and 75 c.c. are titrated as before. The difference between the results of the two titrations, after allowing for 25 c.c. not used in the second case, gives the amount of picric acid which could combine with half the nicotine present. The method gives concordant figures for analyses of ammoniacal distillates from tobacco.

For a polarimetric method of estimating nicotine in tobacco extracts see Degrazia.<sup>2</sup>

#### ERRATA IN VOL VI.

Page 237, line 9 for "nicotyrin, l-methyl-" read "nictotyrene (l-methyl;" and insert bracket in line 10 after pyrrole.

Page 242, line 2 for "thesk in" read "the skin."

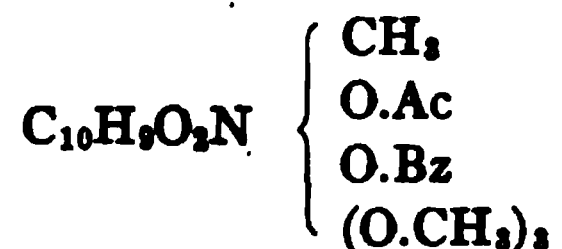
<sup>1</sup> *Gazzetta*, 1913, 43, ii, p. 493.

<sup>2</sup> *Fachl. Mitt. Oesterr. Tabakregie*, 1910, 87, and 149; *Chem. Zentr.*, 1911, 1, 1085 and 1086.

# ACONITE ALKALOIDS.

By FRANCIS H. CARR.

**The Alkaloids of Aconitum Napellus.**—Our knowledge of the constitution of aconitine—the chief of the aconite alkaloids—has made some very slight progress since the publication of Vol. VI. This is due principally to work on its oxidation. It has been shown by one worker<sup>1</sup> that when aconitine is oxidised with permanganate in acid solution, acetaldehyde and a neutral substance, *oxonitin*,  $C_{23}H_{29}O_9N$ , m. p.  $274^\circ$ , are produced. Another worker,<sup>2</sup> while confirming this, has expressed the view that when neutral permanganate is employed, a substance of similar properties, but having the formula  $C_{24}H_{29}O_9N$ , is produced. It appears likely that further investigation will establish the identity of these two compounds.<sup>3</sup> Oxonitin retains three methoxyl groups as well as the N-methyl, benzoyl and acetyl groups of aconitine. It may be represented:



On hydrolysis, acetic and benzoic acids are split off and an alkaloid, soluble in ether, remains.

By the action of nitric acid a yellow crystalline substance  $C_{22}H_{26}O_{11}N$ ,<sup>4</sup> m. p.  $205^\circ$ , results. It contains a nitroso and two carboxyl groups.

A substance  $C_{22}H_{43}O_9N$  prepared by heating aconitine in a similar manner to that employed by Dunstan and Carr for pyraconitine has been described by Schulze and Liebner.<sup>5</sup> Its properties, however, differ considerably from those of pyraconitine and it would appear to be a new alkaloid. The new base melts at  $171^\circ$  and has  $[\alpha]_D$  in alcohol  $-112^\circ$ . Pyraconitine melts at  $167^\circ$ – $168^\circ$  and its solution in alcohol is optically inactive. The *hydrobromide* of the new base melts at  $240^\circ$  and has  $[\alpha]_D$  in water  $-106^\circ$ . Pyraconitine hydrobromide melts at  $280^\circ$ , and has  $[\alpha]_D$  in water  $-47^\circ$ . The *hydrochloride* of the new base melts at  $170^\circ$ , and that of pyraconitine melts at  $249^\circ$ .

<sup>1</sup> Carr, *Trans.*, 1912, 101, 2241.

<sup>2</sup> Brady, *Trans.*, 1913, 103, 1821.

<sup>3</sup> Barger and Field (*Trans.*, 1915, 107, 231) have later established the identity of these substances and suggested other formulæ.

<sup>4</sup> Brady, *Trans.*, 1913, 103, 1821.

<sup>5</sup> *Arch. Pharm.*, 1913, 251, 453.

**The Alkaloids of Aconitum Vulparia** (*A. Lycoctonum* of authors).—The previous work on these alkaloids has been considerably added to and modified by Schulze and Bierling:<sup>1</sup>

**Lycaconitine.**—The formula of this alkaloid is now to be regarded as  $C_{36}H_{46}O_{10}N_2$ . It is a weak base and has  $[\alpha]_D$  in alcohol  $+42.5^\circ$ . No crystalline salt could be prepared. By acid hydrolysis it yields succinic acid and anthranoyl-lycoctonine. Alkaline hydrolysis produces lycoctonine and lycoctonic acid.

**Myoctonine**, according to the new work, has the formula  $(C_{36}H_{46}O_{10}N_2)_2$ . It will not crystallise, and no crystalline derivatives could be prepared. It has  $[\alpha]_D +44.8^\circ$  in alcohol. This alkaloid yields lycoctonine and lycoctonic acid on hydrolysis by acids or alkalis.

**Lycoctonine**  $C_{25}H_{39}O_7N \cdot H_2O$ , has different properties from those previously ascribed to the hydrolytic alkaloid which has also been named *Lyaconine*. It is well crystallised and colourless; it melts at  $131^\circ-133^\circ$ , and has  $[\alpha]_D +49.6^\circ$  in alcohol. It contains four methoxyl-, a methylimino- and two hydroxy groups. It is a strong base, and forms crystalline salts. The *hydrochloride*,  $(B.HCl, H_2O)$ , forms prisms, m. p.  $75^\circ$ ; the *hydrobromide*,  $(B.HBr, 2H_2O)$ , melts at  $88^\circ-89^\circ$ .

**Lycoctonic acid**.  $C_{11}H_{11}NO_6$ , appears to be succinanylcarboxylic acid



**Anthranoyl-lycoctonine**,  $C_{32}H_{44}O_8N_2$ , which results from the acid hydrolysis of lycaconitine, melts at  $154^\circ-155^\circ$ . It forms brown leaflets readily soluble in chloroform, but less so in other solvents. It yields lycoctonine and anthranilic acid on alkaline hydrolysis.

All the alkaloids of this group exert powerful toxic effects on the heart; 0.01 grm. of lycaconitine and of myoctonine suffice to stop the frog's heart in 7 hours.

**Assay of Aconite and its Preparations.**—In the British Pharmacopœia, 1914, an alkaloidal standard for aconite root and its preparations is introduced. The following method of assay is directed for the root:

Into a small stoppered glass percolator, provided with a glass tap and suitably plugged with cotton wool, introduce 10 grm. of aconite root in No. 40 powder and 75 c.c. of alcohol (70%). Macerate for 4 hours, shaking occasionally. Then allow percolation to proceed slowly until the liquid ceases to drop. Continue the percolation by the addition of more of the same menstruum until 150 c.c. have been collected or the root is exhausted. Evaporate the percolate to dryness in a shallow porcelain evaporating basin, at a temperature not exceeding  $60^\circ$ . Dissolve the residue in 5 c.c. of *N*/10 solution of sulphuric acid diluted with 20 c.c. of water. Filter into a separating funnel, washing the dish, and filter with about 30 c.c. of water. Add

<sup>1</sup> *Arch. Pharm.*, 1913, 251, 8.

to the mixed filtrate and washings 25 c.c. of ether and 2 c.c. of solution of ammonia, and shake for 1 minute. After separation draw off the lower layer into a flask, and filter the ethereal solution into a beaker. Return the contents of the flask to the separator, add 20 c.c. of ether and again shake for 1 minute, separating the aqueous liquid and filtering the ethereal solution into the beaker. Repeat the operation with two other portions, each of 20 c.c. of ether. Evaporate the mixed ethereal solutions to dryness, dry the residue at 60°, dissolve it in 5 c.c. of *N*/20 solution of sulphuric acid diluted with 20 c.c. of water, and titrate back with *N*/20 solution of sodium hydroxide, tincture of cochineal being used as indicator. Deduct the number of c.c. of the alkaline solution required from 5, multiply the difference by 0.3217; the result will be the percentage of ether-soluble alkaloids in the powdered root.

The Pharmacopœia requires that the root shall contain not less than 0.4% of alkaloid when assayed by the above process and that the tincture shall be standardised to contain 0.04%.

Attention<sup>1</sup> has been drawn to the importance attaching to the comparison of weight and titration values; the theoretical figure 0.06434 grm. per c.c. of *N*/10 acid is frequently exceeded, showing that other bases are present. It is to be observed that it is important to extract the acid aqueous liquor with ether very completely before rendering alkaline to extract the alkaloid and that the acidity of this liquor should not, at the same time, be excessive.

**Toxicological Detection of Aconite.**—Fühner<sup>2</sup> points out that in forensic cases aconitine may best be detected by observing its action upon the isolated frog's heart. The peristalsis shown on the tracings is characteristic. 0.005 mg. may be detected in this way. While the tingling on the tongue is a valuable indication, a similar effect, though weaker, is produced by veratrine.

<sup>1</sup> Evan's Analytical Notes, 1911, 12 and 13.

<sup>2</sup> *Arch. Exp. Path. Pharm.*, 1911, 66, 178.

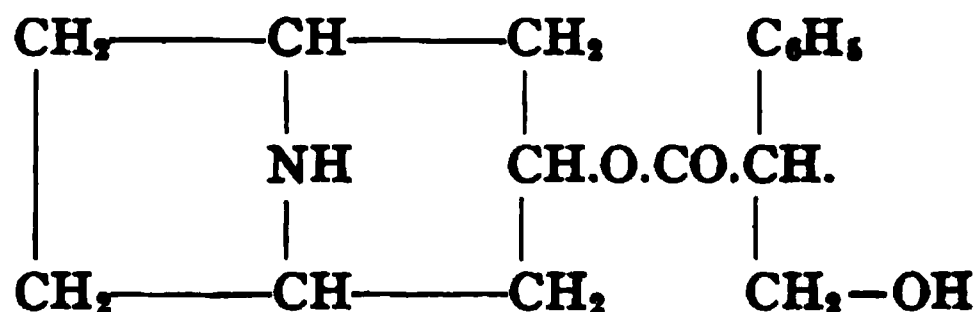
# ATROPINE AND ITS ALLIES.

By FRANCIS H. CARR.

## TROPEINES AND SCOPOLEINES.

Their constitution being well known, the chemistry of atropine and hyoscyamine has undergone little advance since the publication of Vol. VI. The new derivatives which have been described, such as the sulphuric acid esters<sup>1</sup> and the methyl methosulphites<sup>2</sup> do not, from their character, call for further description in the present work.

The alkaloid pseudo-hyoscyamine which was previously regarded as an isomer of atropine and hyoscyamine, has been shown<sup>3</sup> to differ in composition from these alkaloids. It is devoid of the methyl group attached to the nitrogen atom, having the formula  $C_{16}H_{21}O_2N$  and it has consequently been renamed *norhyoscyamine*. Its racemic modification noratropine has also been prepared by Carr and Reynolds. When hydrolysed with alkalis, these alkaloids yield nortropanol and tropic acid. They may be represented by the formula



Noratropine and norhyoscyamine react readily with methyl iodide, forming atropine and hyoscyamine respectively, and by using other alkyl iodides homologous N-alkyl derivatives are formed.

**Hyoscine.**—The constitution of hyoscine (scopolamine) remains unknown, but the work of Willstätter and his collaborators<sup>4</sup> indicates that one of the oxygen atoms of scopoline (the base derived by hydrolysis) is attached by an ether-like linking, the other being present as an hydroxyl. Further, Tutin<sup>5</sup> has shown that scopoline may be obtained in its optically active form, and must contain either one or two asymmetric carbon atoms; if the latter be the case, the asymmetric groupings must be similar.

The following new substances in this group of alkaloids call for further description.

<sup>1</sup> Hoffman La Roche & Co., D.R.P., 247455 and 247457.

<sup>2</sup> Gerber, D.R.P., 228204.

<sup>3</sup> Carr and Reynolds, *Trans.*, 1912, 101, 974.

<sup>4</sup> *Zeit. physiol. Chem.*, 1912, 79, 146.

<sup>5</sup> *Trans.*, 1910, 97, 1793.

**Noratropine**,  $C_{16}H_{21}O_2N$ , is a white crystalline base, m. p.  $113^{\circ}$ – $114^{\circ}$ ; it readily combines with water, forming a monohydrate, m. p.  $73^{\circ}$ . Noratropine and its salts are optically inactive.

**Noratropine hydrochloride**,  $(B, HCl)$ , crystallises from a mixture of alcohol and acetone in silky needles m. p.  $193^{\circ}$ ; **noratropine sulphate**,  $(B_2, H_2SO_4)$ , separates from water in long needles, m. p.  $257^{\circ}$ ; **noratropine aurichloride**,  $(B, HAuCl_4)$ , forms rosettes of leaflets which melt under hot water, and crystallise on cooling, m. p.  $157^{\circ}$ .

**Norhyoscyamine**,  $C_{16}H_{21}O_2N$ , has been shown by Carr and Reynolds<sup>1</sup> to occur in *Datura metel* 0.01%, *Datura meteloides* 0.02%, *Duboisia myoporoides* 0.15% and *Scopolia japolica* 0.03%. These authors also point out that there is evidence to show that it occurs in *Datura fastuosa* and *Mandragora vernalis*. Norhyoscyamine crystallises in prismatic needles, m. p.  $145.5^{\circ}$ . The specific rotatory power of the pure base in 50% alcohol is  $[\alpha_D] - 23.0$ .

**Norhyoscyamine hydrochloride**,  $(B, HCl)$ , forms rosettes of needles from alcohol and ether, m. p.  $207^{\circ}$ , **norhyoscyamine sulphate**,  $(B_2, H_2SO_4, 3H_2O)$ , crystallises from acetone and water in long slender silky needles, m. p.  $249^{\circ}$ ; **norhyoscyamine aurichloride**,  $(B, HAuCl_4)$ , separates from alcohol and water in glistening golden yellow scales, m. p.  $178^{\circ}$ – $179^{\circ}$ .

**Detection and Estimation of Tropeines.**—It has been pointed out that the properties of the gold salts and picrates of these alkaloids constitute the best means of identifying them when sufficient substance is available. Carr<sup>2</sup> shows that when working with pure alkaloid  $\frac{1}{10}$  grain may be identified by the aurichloride and  $\frac{1}{50}$  grain by the picrate method.

The following table gives the melting point of the chief salts of the alkaloids of this group.

	Hyoscyamine	Atropine	Norhyoscyamine	Noratropine	l-Hyoscyne	i-Scopolamine
Alkaloid.....	107°	116–117°	140.5°	113–114°	.....	.....
Hydrochloride.....	.....	163	207	193	200°	.....
Sulphate.....	205–209	194	249	257	.....	.....
Oxalate.....	176	196–197	245	247–248	.....	.....
Aurichloride.....	165	137–139	178–179	157	198–200	208°
Picrate.....	165–166	175–176	220	227	180–181	193

The test for atropine and hyoscyamine described in paragraph g, on page 307 of Vol. VI has been modified by Labat.<sup>3</sup> A particle of the alkaloid is placed in a test-tube and 2 c.c. of 10% sulphuric acid and 1 drop of a saturated aqueous solution of potassium chromate added. On warming, the characteristic hawthorn odour develops and changes to the odour of benzaldehyde. The latter odour is also produced when the alkaloid is boiled with a dilute solution of sodium hypobromite.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Chem. World*, 1, 3.

<sup>3</sup> *Bull. Soc. Pharm. Bord.*, April, 1914, 148

For the assay of belladonna leaves the British Pharmacopœia 1914 gives the following method:

Into a small stoppered glass percolator provided with a glass tap and suitably plugged with cotton wool, introduce 10 grm. of belladonna leaves in No. 60 powder, and 50 c.c. of a mixture of chloroform 1 volume and ether 4 volumes. Shake, set aside for 10 minutes, then add 2 c.c. of solution of ammonia diluted with 3 c.c. of water, and set aside for 1 hour, shaking frequently. Then allow percolation to proceed slowly, receiving the percolate in a separator containing 6 c.c. of  $N/1$  solution of sulphuric acid diluted with 20 c.c. of water. When the liquid ceases to pass, continue the percolation with a further 50 c.c. or more of the ether-chloroform mixture, added in small quantities until the leaves are exhausted. Shake the separator well, and, after separation, draw off the acid liquid into a second separator. Repeat the extraction of the ether-chloroform solution with two successive portions, each of 10 c.c. of the diluted acid. Make the mixed acid solution alkaline with solution of ammonia, and shake out with three successive portions of 15, 15, and 5 c.c. of chloroform. Evaporate the mixed chloroform solutions to dryness, dissolve the residue in 3 c.c. of ether, and again evaporate to dryness. Dissolve the residue in 10 c.c. of  $N/20$  solution of sulphuric acid and titrate with  $N/20$  solution of sodium hydroxide, tincture of cochineal being used as an indicator. Deduct the number of c.c. of the alkaline solution required from 10, multiply the difference by 0.1446; the product will be the percentage of alkaloids in the leaves.

The method given for the assay of liquid extract of belladonna in the 1914 B. P. is similar to that given in the previous B. P. but omits the first alkaline extraction. The following method is given for the assay of dry extract of belladonna, tincture of belladonna and extract of hyoscyamus:

Evaporate 100 c.c. in an evaporating basin on a water-bath, until it measures about 10 c.c., add, if necessary, sufficient alcohol (90%) to dissolve any separated substance, and transfer to a separator, rinsing the dish with a little water. Add 10 c.c. of water, 20 c.c. of chloroform, and 2 c.c. of solution of ammonia. Shake well and separate the chloroform layer. Repeat the extraction with two successive portions of 10 c.c. of chloroform. Mix the chloroform solutions, and shake them with 10 c.c. of  $N/1$  solution of sulphuric acid, diluted with twice its volume in water. Separate the chloroform solution. Repeat the shaking with a further 10 c.c. of the acidified water. Mix the acid solutions, add 20 c.c. of chloroform and 4 c.c. of solution of ammonia. Shake well, draw off the chloroform solution into a beaker, and repeat the extraction with two further portions, each of 10 c.c. of chloroform. Allow the mixed chloroform solutions to evaporate, dry the residue on a water-bath 30 minutes, dissolve it in 10 c.c. of  $N/20$  solution of sulphuric acid and titrate with  $N/20$  solution of sodium hydroxide, using tincture of cochineal as indicator. Deduct the number of c.c. of alkaline solution required from 10, and multiply the difference by 0.01446; the prod-



It will be the weight in grams of the alkaloids contained in 100 c.c. of the tincture.

The B. P., 1914, adopts the following standards:

Belladonna leaves	Not less than 0.3 % of alkaloid.
Belladonna root	No standard.
Belladonna plaster	0.25 % of alkaloid.
Belladonna ointment	0.6 % of alkaloid.
Ext. of belladonna dried	0.95 to 1.05 % of alkaloid.
Ext. of belladonna liquid	0.75 % w/v of alkaloid.
Ext. of hyoscyamus	0.3 % of alkaloid.
Tinct. of belladonna	0.035 % w/v of alkaloid.

A suggestion<sup>1</sup> has been made that for the determination of atropine the insoluble silicotungstate should be precipitated and weighed. The salt is soluble less than 1 part in 40,000 and has the composition  $12\text{WO}_3, \text{SiO}_2, \text{H}_2\text{O}, 4\text{B}$ , after drying at  $20^\circ$ .

#### ERRATA IN VOL. VI.

Page 256, last line, for "acetyl" read "acyl."

Page 297, last line, for "page 291" read pages 291 and 303."

Page 298, line 6 from bottom, for "Atropamine.—Apo-atropine" read "Atropamine-Apo-atropine."

Page 299, line 3 from bottom, "page 291" should read "pages 289 and 290."

<sup>1</sup> O. Javillier, *Bull. Sci. Pharm.*, 1910, 315

# COCAINE.

By SAMUEL P. SADTLER.

**Separation and Identification of Cocaine.**—H. C. Fuller<sup>1</sup> gives the following method:

Solid substances are dissolved in water or in *N/1* sulphuric acid, or if necessary they are extracted with alcohol containing ammonia, water is added, and the bulk of the alcohol evaporated. Syrups should be diluted to the consistence of a 50% sugar solution and freed from gum and fat when present. The solution, containing a slight excess of ammonia, is shaken in a separating funnel with three successive portions of 50 c.c. of *Prolius* mixture (ether 4 parts, chloroform 1 part, alcohol 1 part), and the combined extracts are filtered and evaporated nearly to dryness on a hot water-bath. The moist residue is taken up with 25 c.c. of *N/1* sulphuric acid, added in portions of not more than 10 c.c., the mixture being warmed and filtered after each addition, and is finally washed with a little water. The acid solution is shaken with five successive portions (15 c.c. each) of chloroform, and the united chloroform extracts washed with 10 c.c. of water, which is added to the acid solution, whilst the chloroform is discarded. The acid solution is next shaken with 10 c.c. of petroleum benzin (b. p. 40–60°), the extract discarded, a slight excess of ammonia added to the acid solution, and the extraction thrice repeated with 15 c.c. of benzin each time. The united benzin extracts are washed once with water, filtered, and evaporated rapidly on the water-bath in a current of air. The residue will then contain any cocaine that was originally present. A test is made for alkaloids in a portion of the residue with mercuric iodide solution, and if a precipitate is obtained the remainder of the residue is heated with 2 c.c. of strong nitric acid on the water-bath until there is no further odour of nitric acid, and then cooled and treated with 5 to 10 drops of *N/5* alcoholic potassium hydroxide solution. On gently warming the dish, cocaine, when present even in minute traces, gives off the odour of ethyl benzoate. A purple colouration indicates the presence of atropine, strychnine or yohimbine, though in some instances a similar colouration is given by the residue from the coca leaf. An odour of ethyl benzoate is also produced by tropacocaine, benzoylecgonine and aconitine, but the first two may be differentiated by means of the microscope, whilst benzoylecgonine and aconitine are not removed to any great extent from the aqueous solution by benzin. Cocaine

<sup>1</sup> *Techn. Division of Drugs, U. S. Dept. Agric., Bureau of Chem., Bull. 150, April 22, 1912, 41–43.*

may also be identified by the crystalline compound which it gives with gold chloride. Moreover, when heated for 1½ hours in a strong closed flask on the water-bath with 15 c.c. of dilute hydrochloric acid and a few crystals of salicylic acid, cocaine will give rise to an odour of oil of wintergreen, whereas tropacocaine does not give this reaction. This test might also indicate cinnamylcocaine and the truxillins, but, on the other hand, none of these gives the ethyl benzoate reaction.

**Differentiation of Cocaine from Its Substitutes.**—D. Sherbatshev<sup>1</sup> describes the following method. Three reagents are required: (1) 10% aqueous solution of ammonia; (2) aqueous potassium hydroxide (1:10); (3) saturated aqueous sodium hydrogen carbonate. Three drops of the solution under examination are placed separately on an object glass by means of a glass rod. To one of these drops is added a drop of solution No. 1, to the second a drop of No. 2, to the third a drop of No. 3. A precipitate may or may not be formed in one or all cases. A transitory precipitate (*i.e.*, one sol. in excess of reagent) is not to be considered a precipitate. In the event of the presence of any of the following compounds, the following are the indications:

	NH <sub>4</sub> OH	KOH	NaHCO <sub>3</sub>
Stovaine.....	Ppt.	Ppt.	Ppt.
β-Eucaine.....	.....	Faint ppt.	.....
Nirvanine.....	Ppt.	Ppt. dissolves	Ppt.
Alpine.....	Ppt.	Ppt.	.....
Holocaine.....	Ppt.	Ppt.	Ppt.
Novocaine.....	.....	Ppt.	.....

Stovaine and holocaine yield precipitates with each reagent. However, since holocaine is little used on account of its toxicity, a precipitate with each reagent is strongly indicative of stovaine. The behaviour of β-eucaine and novocaine is likely to mislead, since the faint precipitate yielded by the former is not sufficiently characteristic.

<sup>1</sup> *Apoth. Ztg.*, 27, 441.

# OPIUM ALKALOIDS

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By FRANK O. TAYLOR.

The short time that has elapsed since the publication of Vol. VI renders any extensive revision of the chapter on Opium Alkaloids unnecessary, although there has been no diminution of work on analytical processes applicable to opium and its alkaloids during the past 3 years, as compared with preceding years. Quite a little new work has been published, but no very radical changes of former methods are involved and the exact estimation of morphine either in opium or in medicinal compounds remains one of the most difficult of all the alkaloidal assays, and the most fruitful in provoking discussion and criticism. The writer will endeavour to give sufficient information regarding new tests or modifications of old methods to permit of their satisfactory use, but detailed discussion cannot be attempted in most instances, and it seems unnecessary to refer to any published papers which do not present any really new material. For convenience of reference the subheads of this chapter will be identical with those in Vol. VI, and the page numbers will frequently be referred to as an added help in connecting this new material with the old.

**Constitution of Opium Bases** (Vol. VI, 355-361).—Some additional work has been done on the constitution of the opium alkaloids and their derivatives, but as this does not necessitate any pronounced change in statements already made and has no bearing on analytical processes there is no need to embody certain of these theoretical considerations in this chapter.

**Behaviour of Opium Bases with Solvents** (Vol. VI, 362).—Some older work not referred to in Vol. VI is that of Schindelmeiser<sup>1</sup> on the solvent action of carbon tetrachloride on alkaloids, among which the following determinations should be recorded here. The figures are grm. dissolved in 100 c.c. at 17°: Morphine 0.032 grm., codeine 1.328 grm., papaverine 0.203 grm., narceine 0.011 grm.

The solubility of morphine and narcotine in acetone, water and mixtures of these has been investigated by Guerin<sup>2</sup> who used these solubilities as the basis of a modified opium assay (see page 505).

Figures indicate amount dissolved in 1000 c.c. at 15°.

<sup>1</sup> *Chem. Zeit.*, 1901, 25, 129.

<sup>2</sup> *J. Pharm. Chim.*, 1913, 7, 438.

	Anhydrous acetone	Acetone and water, equal parts	Water
Morphine.....	1.28 gm.	1.32 gm.	0.288 gm.
Narcotina.....	41.96 gm.	0.70 gm.	0.1 gm.

For new determinations on dionin see that heading.

**Colour Reactions of Opium Bases** (Vol. VI, 366–370).—For several new colour reactions, some of which are quite useful, see under the proper alkaloidal headings.

**Salts of Morphine** (Vol. VI, 376–379).—*Morphine sulphate* as obtained commercially has been found frequently to contain considerable amounts of codeine sulphate as an impurity. Engelhardt and Jones<sup>1</sup> in four samples found from 1.45% to 3.97%, and Williams<sup>2</sup> in five samples found from 0.9% to 7.0%, while in tablets he found codeine sulphate to the extent of 2.5% to 6.5% of the morphine sulphate present. He demonstrated that morphine when precipitated from even a dilute solution containing codeine was liable to carry a part of the codeine along with it, thus accounting for its presence in commercial morphine salts. For method of estimation see under the sections on Codeine.

Engelhardt and Winters<sup>3</sup> compare several methods of estimating the purity of morphine salts and find that morphine nitrate rarely runs above 90% of the theoretical purity; they do not indicate what the impurities are or whether this is solely a case of a different amount of water of crystallisation than is ordinarily calculated. They find morphine acetate also contains somewhat below 100% of the theoretical strength.

**Detection and Estimation of Morphine** (Vol. VI, 379–387).—This section as in Vol. VI deals chiefly with qualitative tests, though some of them are capable of elaboration for roughly quantitative work.

Fabinyi<sup>4</sup> reports on a colour test for morphine originally devised by Radulescu as follows: To the solution to be tested add a few drops of dilute hydrochloric or sulphuric acid, then a very small quantity of sodium nitrite either in dry form or solution, and finally make alkaline with either ammonia or sodium or potassium hydroxide. In the presence of morphine a red colour at once appears which is destroyed by acid and restored by alkali. When the solution is very dilute the colour is more of a mahogany shade. In strong solutions a green colour is produced on adding the sodium nitrite and before the alkali is added. The same test is reported on by Radulescu<sup>5</sup> who tried it on 150 substances and found but one (a lettuce extract of doubtful purity) that gave a similar indication. He considers that the colour probably depends on the formation of nitroxanthranol. This colour is not extracted by chloroform, carbon disulphide or ether. The test has the great advantage of

<sup>1</sup> *Drug. Circ.*, 1911 555.

<sup>2</sup> *Am. J. Pharm.*, 1912, 84, 391.

<sup>3</sup> *J. Am. Pharm. Assoc.*, 1915, 4, 288.

<sup>4</sup> *Oesterr. Chem. Zeit.*, 1912, 15, 61.

<sup>5</sup> *Boll. chim. farm.*, 1913, 51, 865.

being applicable to many compounds without extracting the morphine in approximately pure form. The writer has had so far only a limited experience with the test but has verified its usefulness in showing the presence of morphine directly in solutions of compound tablets and in mixtures such as Tr. opium camphorated. It accurately distinguishes morphine from codeine and dionin, which give no colour with the test, but is not so dependable in the case of heroin as this substance gives a slight colour almost identical with that of morphine in very dilute solution, so by this test alone one cannot be certain whether there is present only a minute quantity of morphine or a large amount of heroin. With equal amounts of the two the colour from the morphine is very much more intense. This test also distinguishes morphine from apomorphine, which alkaloid gives a peculiar and characteristic reaction described under apomorphine (page 499).

Aloy and Rabaut<sup>1</sup> report further experiments on the test with uranium acetate or nitrate (see Vol. VI, 386). It is preferable to add a small crystal of uranium nitrate to the solutions under test rather than a 5% solution. They now claim it will detect as little as 0.05 mg. of morphine, but to do so the conditions must be the best possible and it is not so delicate as a number of other tests; furthermore it is not characteristic of morphine but is given by many substances which contain a phenolic hydroxyl group.

Oliver has very recently<sup>2</sup> described as a new test one based on the catalytic action of copper, apparently being unaware that Denigès in 1910 published what is practically the same test (see Vol. VI, 386). However, his peculiar method of applying it seems to render it more delicate than in the form originally proposed by Denigès, or at least this is indicated by the writer's brief experience with the modified test. To the solution under test add 1 or 2 c.c. of hydrogen peroxide solution and sufficient 28% ammonia to make distinctly alkaline, and stir with a bright copper wire when a port wine or dark cherry colour quickly develops. The use of the wire enables a more delicate adjustment of the test than by the use of copper sulphate solution. To render it more delicate add a little solution of potassium cyanide after stirring with the copper wire, to destroy any blue colour from the copper and ammonia. The test will detect in a pure solution as little as 0.02 mg. of morphine. The writer has verified the statement of Denigès, which is contrary to that of Oliver, that heroin gives a similar indication; in fact this alkaloid responds to the test even more quickly than morphine and the colour is almost identical. Codeine and dionin give no colour, but apomorphine gives a raspberry red that fades rather quickly.

The peculiar effect of morphine on white mice is made the basis of a biological test by Hermann.<sup>3</sup> These animals treated hypodermically with morphine become abnormally active and excitable, especially to noises, and the tail assumes an S-shaped curve over the back. It is stated that 5 mg. gives

<sup>1</sup> *Bull. Soc. Chim.*, 1914, 15, 680.

<sup>2</sup> *Med. Chronicle*, 1914, 27, 221.

<sup>3</sup> *Biochem. Zeit.*, 1912, 39, 216.

a reaction in 2 minutes which persists over 20 hours, and 0.01 mg. showed an effect in 12 minutes which lasted 1-2 hours. This test is not specially useful but can be employed to check preliminary solutions obtained in forensic work.

**Apomorphine** (Vol. VI, 387-389).—In the course of certain experiments V. Paolini<sup>1</sup> found that the hydrochloride contained an average amount of 4.2% of water or 0.75 H<sub>2</sub>O in each molecule. He also prepared a *dibenzoate*, m. p. 156°, by the action of benzoyl chloride in presence of pyridine.

The formation of apomorphine in morphine solutions (see Vol. VI, 388) has been carefully investigated by Feinberg<sup>2</sup> who finds it is not produced by long-continued boiling of solutions of morphine, its hydrochloride or other salts, nor by long standing either with or without the presence of nutrient media to promote bacterial action.

Feinberg also describes a test for apomorphine in presence of morphine. To a solution add 3 drops of 1% solution of potassium ferricyanide and shake with 1 c.c. of benzene. In presence of apomorphine the benzene is coloured amethyst-violet, and on adding a few drops of sodium hydroxide solution and shaking, the colour changes to violet-red and, on long standing, to violet. This is a very delicate test, but it is not at all necessary to use the ferricyanide, as the addition of a few drops of ammonia and shaking with benzene gives the same results, only a little more slowly.

On making a solution of apomorphine slightly acid with hydrochloric or sulphuric acid and then adding a very little sodium nitrite, a magnificent deep cherry-red colour appears. The colour is best shown in very dilute solution and with small quantities of reagents. The test serves not only to distinguish apomorphine from morphine, but will detect a very small amount of the former in the presence of much morphine. No colour is imparted to ether or chloroform on shaking with them, but on adding ammonia the colour changes to a dirty green, and then on shaking with ether or chloroform these solvents assume the characteristic violet colour derived from apomorphine as in the preceding test.

The test given in Vol. VI, p. 389, for  $\beta$ -chloromorphide in apomorphine should specify a solution of sodium bicarbonate instead of the carbonate.

**Heroin** (Vol. VI, 389).—The colour test with hexamethylene-tetramine and sulphuric acid is best applied by using as a reagent 10 c.c. of the concentrated acid mixed with about 0.5 c.c. of 10% solution of hexamethylene-tetramine. To a few c.c. of this, add either a crystal of heroin or its salts or a very little solution, when a fine purplish or violet colour at once appears. This is not characteristic, as morphine and codeine give similar colours as do other substances of a phenolic character. The test is practically identical with that given by formaldehyde and sulphuric acid.

In the absence of morphine or other interfering substances Miller<sup>3</sup> uses

<sup>1</sup> *Atti. accad. Lincei*, 1913, 22, II, 121; *Chem. Abst.*, 1914, 79.

<sup>2</sup> *Zeit. physiol. Chem.*, 1913, 84, 363.

<sup>3</sup> *Am. J. Pharm.*, 1915, 87, 248.



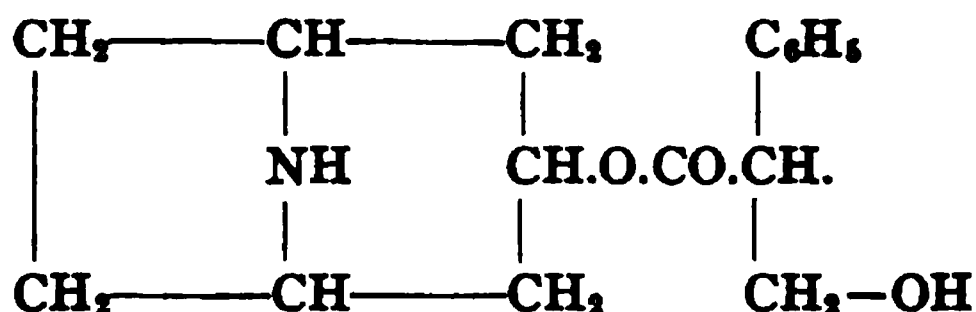
# ATROPINE AND ITS ALLIES.

By FRANCIS H. CARR.

## TROPEINES AND SCOPOLEINES.

Their constitution being well known, the chemistry of atropine and hyoscyamine has undergone little advance since the publication of Vol. VI. The new derivatives which have been described, such as the sulphuric acid esters<sup>1</sup> and the methyl methosulphites<sup>2</sup> do not, from their character, call for further description in the present work.

The alkaloid pseudo-hyoscyamine which was previously regarded as an isomer of atropine and hyoscyamine, has been shown<sup>3</sup> to differ in composition from these alkaloids. It is devoid of the methyl group attached to the nitrogen atom, having the formula  $C_{16}H_{21}O_2N$  and it has consequently been renamed *norhyoscyamine*. Its racemic modification noratropine has also been prepared by Carr and Reynolds. When hydrolysed with alkalis, these alkaloids yield nortropanol and tropic acid. They may be represented by the formula



Noratropine and norhyoscyamine react readily with methyl iodide, forming atropine and hyoscyamine respectively, and by using other alkyl iodides homologous N-alkyl derivatives are formed.

**Hyoscine.**—The constitution of hyoscine (scopolamine) remains unknown, but the work of Willstätter and his collaborators<sup>4</sup> indicates that one of the oxygen atoms of scopoline (the base derived by hydrolysis) is attached by an ether-like linking, the other being present as an hydroxyl. Further, Tutin<sup>5</sup> has shown that scopoline may be obtained in its optically active form, and must contain either one or two asymmetric carbon atoms; if the latter be the case, the asymmetric groupings must be similar.

The following new substances in this group of alkaloids call for further description.

<sup>1</sup> Hoffman La Roche & Co., D.R.P., 247455 and 247457.

<sup>2</sup> Gerber, D.R.P., 228204.

<sup>3</sup> Carr and Reynolds, *Trans.*, 1912, 101, 974.

<sup>4</sup> *Zeit. physiol. Chem.*, 1912, 79, 146.

<sup>5</sup> *Trans.*, 1910, 97, 1793.

**Noratropine**,  $C_{16}H_{21}O_2N$ , is a white crystalline base, m. p.  $113^{\circ}$ – $114^{\circ}$ ; it readily combines with water, forming a monohydrate, m. p.  $73^{\circ}$ . Noratropine and its salts are optically inactive.

**Noratropine hydrochloride**,  $(B, HCl)$ , crystallises from a mixture of alcohol and acetone in silky needles m. p.  $193^{\circ}$ ; **noratropine sulphate**,  $(B_2, H_2SO_4)$ , separates from water in long needles, m. p.  $257^{\circ}$ ; **noratropine aurichloride**,  $(B, HAuCl_4)$ , forms rosettes of leaflets which melt under hot water, and crystallise on cooling, m. p.  $157^{\circ}$ .

**Norhyoscyamine**,  $C_{16}H_{21}O_2N$ , has been shown by Carr and Reynolds<sup>1</sup> to occur in *Datura metel* 0.01%, *Datura meteloides* 0.02%, *Duboisia myoporoides* 0.15% and *Scopolia japolica* 0.03%. These authors also point out that there is evidence to show that it occurs in *Datura fastuosa* and *Mandragora vernalis*. Norhyoscyamine crystallises in prismatic needles, m. p.  $145.5^{\circ}$ . The specific rotatory power of the pure base in 50% alcohol is  $[\alpha_D] - 23.0$ .

**Norhyoscyamine hydrochloride**,  $(B, HCl)$ , forms rosettes of needles from alcohol and ether, m. p.  $207^{\circ}$ , norhyoscyamine sulphate,  $(B_2, H_2SO_4, 3H_2O)$ , crystallises from acetone and water in long slender silky needles, m. p.  $249^{\circ}$ ; norhyoscyamine aurichloride,  $(B, HAuCl_4)$ , separates from alcohol and water in glistening golden yellow scales, m. p.  $178^{\circ}$ – $179^{\circ}$ .

**Detection and Estimation of Tropeines.**—It has been pointed out that the properties of the gold salts and picrates of these alkaloids constitute the best means of identifying them when sufficient substance is available. Carr<sup>2</sup> shows that when working with pure alkaloid  $\frac{1}{10}$  grain may be identified by the aurichloride and  $\frac{1}{50}$  grain by the picrate method.

The following table gives the melting point of the chief salts of the alkaloids of this group.

	Hyoscyamine	Atropine	Norhyoscyamine	Noratropine	l-Hyoscyne	i-Scopolamine
Alkaloid.....	$107^{\circ}$	$116$ – $117^{\circ}$	$140.5^{\circ}$	$113$ – $114^{\circ}$	.....	.....
Hydrochloride.....	.....	163	207	193	$200^{\circ}$	.....
Sulphate.....	205–209	194	249	257	.....	.....
Oxalate.....	176	196–197	245	247–248	.....	.....
Aurichloride.....	165	137–139	178–179	157	198–200	$208^{\circ}$
Picrate.....	165–166	175–176	220	227	180–181	193

The test for atropine and hyoscyamine described in paragraph g, on page 307 of Vol. VI has been modified by Labat.<sup>3</sup> A particle of the alkaloid is placed in a test-tube and 2 c.c. of 10% sulphuric acid and 1 drop of a saturated aqueous solution of potassium chromate added. On warming, the characteristic hawthorn odour develops and changes to the odour of benzaldehyde. The latter odour is also produced when the alkaloid is boiled with a dilute solution of sodium hypobromite.

<sup>1</sup> Loc. cit.

<sup>2</sup> Chem. World, 1, 3.

<sup>3</sup> Bull. Soc. Pharm. Bord., April, 1914, 148

In the spectroscope this solution gives an absorption band near the infra-red with a 1:1000 solution.

**Thebaine** (Vol. VI, 405-406).—In *Papaver orientale* Klee<sup>1</sup> has found both thebaine and a new alkaloid which he calls

**Iso-thebaine**,  $C_{17}H_{14}N(OCH_3)_2OH$ , m.p.  $203^{\circ}$ – $204^{\circ}$ ;  $[\alpha]_D = +285.1^{\circ}$  in alcohol. It gives crystalline salts with sulphuric and hydrochloric acids and forms an *L*-bitartrate. On treating with nitric acid it gives an intense violet colour becoming brownish and then reddish-yellow, which is said to be characteristic. It may be separated from thebaine by heating with dilute hydrochloric acid which converts the thebaine into thebenine, insoluble in ether, but does not affect the *iso*-thebaine.

There has recently been a tendency to use for medicinal purposes a mixture of some of the opium alkaloids or their salts in a pure form, owing to the fact, now fairly well established, that morphine alone differs in its physiological action from a mixture with other alkaloids, particularly narcotine, and the analysis of these may be mentioned here.

**Pantopon**, stated to be the hydrochlorides of the combined opium alkaloids, has been examined by Mannich and Schwedes<sup>2</sup> with the following result:

Morphine.....	47.5%	H <sub>2</sub> O.....	9.5%
Narcotine.....	11.2%	HCl.....	9.4%
Codeine.....	6.4%	Mineral substances.....	0.3%
Other opium bases.....	10.9%		

**Opiopon** is a similar preparation, but Mannich and Schwedes found that the composition of two different samples varied greatly.

**Opon** is like the two preceding products except that it contains no morphine.

The estimation of each alkaloid separately, except a few of the most important, is out of the question as it is a matter of extreme difficulty, but for practical purposes the estimation of morphine, narcotine and codeine is sufficient and in some cases that of morphine alone.

Anneler<sup>3</sup> reports on the investigation of several methods of estimating morphine and prefers, of the crystallisation methods tried, that of the British Pharmacopœia (Vol. VI, 423) as modified by Debourdeaux (see page 507). Of the shake-out methods the following is the one that gave the best results which, however, were about 1.5% too high:

Dissolve 0.8 to 1.0 gm. in 30 c.c. of water and add a concentrated aqueous solution containing 1.0 gm. of sodium hydrogen carbonate. Shake out with three 10 c.c. portions of chloroform saturated with morphine, agitating gently to avoid an emulsion. The chloroform solution is drawn off and filtered through paper wetted by chloroform. 60 c.c. of a mixture of equal parts of chloroform and *isobutyl* alcohol are then passed through this same filter into the separator containing the original aqueous solution. Shake for 10 minutes

<sup>1</sup> *Arch. Pharm.*, 1914, 252, 211.

<sup>2</sup> *Apoth. Zeit.*, 1913, 28, 82.

<sup>3</sup> *Arch. Pharm.*, 1912, 250, 186.

and draw off into another separating funnel. Repeat the extraction with 20 and 10 c.c. of the same mixture. The united extracts are then shaken with 10 c.c. of water, the water discarded, the chloroform-*isobutyl* alcohol solution filtered into a clean separator through a filter wet with chloroform. Shake out with 20 c.c. of *N*/10 hydrochloric acid and wash with two 10 c.c. portions of water. Titrate the combined acid solution with *N*/10 alkali, using iodeosin indicator in the presence of 30 c.c. of ether.

**Morphine-narcotine Meconate**, known also under the name **Narcophine**, is a double salt of morphine, containing equi-molecular quantities of morphine, narcotine and meconic acid, with 4 molecules of water of crystallisation. This theoretical constitution is not exactly carried out in practice, as is shown by comparison of the theoretical values and an analysis by Dott<sup>1</sup> shown in the table below:

	Theory	Analysis
Morphine.....	29.38 %	31.3 %
Narcotine.....	42.57 %	38.6 %
Meconic acid.....	20.61 %	24.6 %
Water.....	7.42 %	5.5 %

This difference is probably due to the feebly basic character of narcotine and to the tendency of meconic acid to behave in some respects like a tribasic acid. Narcophine obtained by interaction of the proper proportions of its three constituents in alcohol and precipitation by ether is completely soluble in 12 parts of water at 20°, which solution can be sterilised in the usual way. A physical mixture of the three does not give a clear solution in water. In this connection it is interesting to note that a mixture of  $\frac{1}{4}$  grain (0.016 grm.) of morphine hydrochloride and the same of narcotine hydrochloride gives a clear solution in 1 c.c. of water that soon throws down a crystalline precipitate of narcotine, especially if heated.

An approximate assay of morphine-narcotine meconate may be made according to Dott (*loc. cit.*) by titrating the morphine directly with *N*/10 acid using cochineal as indicator. The end point is not distinct but fairly good results are obtainable, even in the presence of the narcotine and meconic acid. In similar manner the meconic acid may be titrated with *N*/10 alkali using phenolphthaleïn as indicator. From these results the narcotine and water may be calculated.

A more accurate but much longer method is to extract the narcotine by shaking the aqueous solution, made alkaline with ammonia, with four or five large portions of ether, evaporate the ethereal solutions to dryness and weigh or titrate. The morphine is estimated by collecting the crystalline precipitate, washing with alcohol saturated with morphine, drying and weighing or by redissolving the crystals with acid, making alkaline with ammonia and extracting with equal parts of chloroform and *isobutyl* alcohol, and afterwards drying and weighing. By a process of this kind, collecting the crystallised

<sup>1</sup> *Pharm. J.*, 1913 (4), 36, 99.

morphine as first mentioned, Puckner<sup>1</sup> obtained from narcophine, morphine 31.12% and narcotine 44.25% and found, by drying, 7.14% water.

The meconic acid may also be estimated by the colourimetric method described on page 506.

### Opium.

(Vol. VI, 407).

**Alkaloids** (Vol. VI, 408).—Work by Van Itallie and Kerbosch<sup>2</sup> has shown that opium from Asia Minor, Persia, Egypt, China, France and America contained morphine, codeine, narcotine, narceine, thebaine and papaverine, but Indian opium from Bengal, Benares and the so-called Patna opium did not contain papaverine.

Mossler<sup>3</sup> gives results of an extended investigation of the amount of morphine in the capsules of the opium poppy under a number of conditions. The whole air-dried capsules contained 0.1369% of morphine, and those sterilised for half an hour in hot alcohol vapour to destroy ferments contained 0.130%. After the exudations of the latex from the scarified capsules a notable quantity of morphine remains in the capsules. In the ripe capsules the morphine falls to 0.053%.

**Adulteration of Opium** (Vol. VI, 417).—von Friedrichs<sup>4</sup> has investigated the effect of various moulds on opium alkaloids and reports that *Penicillium glaucum* and *Citromyces glaber* do not attack any of the important opium alkaloids. *Aspergillus niger* attacks narcotine and codeine but not morphine, whilst *Aspergillus ostianus*, found especially on Turkish opium, appears to decompose morphine slightly as well as narcotine and codeine.

**Estimation of Morphine in Opium** (Vol. VI, 417-433).—Several investigators have recently called attention to the fact that a portion of the morphine in opium is often in such a condition that it is insoluble in water, so that any assay process that involves preliminary extraction of the opium with water is liable to give low results. (See Debourdeaux,<sup>5</sup> Collard,<sup>6</sup> La Tour and Nal-passe,<sup>7</sup> and Shreve.<sup>8</sup>) Results obtained by Debourdeaux also indicate that in a powdered opium the amount of insoluble morphine increases with age but not at a definite rate, and at the same time the total amount of morphine decreases slightly, probably due to the action of an oxydase. Latour and Nal-passe (*loc. cit.*) state that even dilute alcohol fails to completely extract morphine from opium in all cases, so that Sydenham's laudanum of proper strength cannot be made from an opium of exactly 10% strength. In this same preparation Debourdeaux reported a marked loss of morphine as shown

<sup>1</sup> *Rep. Lab. Am. Med. Assoc.*, 6, 92.

<sup>2</sup> *Arch. Pharm.*, 1911, 248, 609.

<sup>3</sup> *Pharm. Zeit.*, 1914, 59, 600.

<sup>4</sup> *Zeit. physiol. Chem.*, 1914, 93, 276.

<sup>5</sup> *J. pharm. chim.*, 1911, 4, 13; 1912, 6, 491 and 542.

<sup>6</sup> *Yearbook Pharm.*, 1913, 359.

<sup>7</sup> *Ann. Fals.*, 6, 289.

<sup>8</sup> *J. Ind. Eng. Chem.*, 1912, 4, 514.

by assay, with ageing, especially when exposed to the air. A specimen assaying 1.024% morphine in 1908 fell to 0.851 in 1912 and another dropped from 1.071% to 0.883 in the same time. While a precipitate was formed, this contained no perceptible traces of morphine. These results, so far as the writer knows, have not been verified by other workers, and it seems rather extraordinary that so stable an alkaloid as morphine should be decomposed in a preparation such as this while fluid extracts of drugs like ipecac and physostigma show practically no loss of alkaloid in the same length of time.

As far as general methods of estimating morphine are concerned, nothing better than one of the various modifications of the lime process has been devised. That of the B. P., 1898, as modified by Dowzard (Vol. VI, 423 and 425) is excellent (see also Jensen<sup>1</sup>).

The B. P. 1914 assay is practically identical with that of the 1898 edition except that the crystals are dried at 115° instead of 110°. The anhydrous morphine is then dissolved in *N*/10 acid and the excess titrated with *N*/10 alkali instead of directly titrating with acid as formerly.

It is highly probable that the ninth revision of the U. S. P. will abandon the old and cumbersome modified Squibb method in favor of a lime process differing from the Steven's method (Vol. VI, 425) chiefly in the extraction of the opium with water and treatment of this previously concentrated extract with lime, instead of mixing the opium and lime before extracting with water. This method will compare very favorably with the B. P. method in speed and accuracy.

Lyons<sup>2</sup> makes a careful and interesting comparison of the Steven's and eighth revision U. S. P. methods. The new U. S. P. standard will be based on anhydrous instead of crystallised morphine, and for powdered opium is 10% to 10.5% as against 12% to 12.5% in the eighth revision.

A new variation of the lime process suggested by Guerin<sup>3</sup> consists in using a small amount of acetone mixed with the solution from which the morphine is precipitated and in washing the morphine crystals with a saturated solution of the same in acetone. In view of the solubility of morphine in mixtures of water and acetone, as determined by Guerin (page 496), this does not seem advisable and is certainly not so good as the use of ether.

La Wall<sup>4</sup> finds that lactose interferes seriously with the U. S. P., eighth revision, assay, unless titration of the morphine is used, and Debourdeaux reports the same for the lime method (see page 507).

Carles,<sup>5</sup> in an apparent endeavour to obtain thorough precipitation by long standing without the risk of having the morphine contaminated with calcium meconate or its double salt with ammonium, precipitates the calcium as oxalate from the lime solution filtered from the opium and then precipitates the morphine with crystallised sodium carbonate.

<sup>1</sup> *Pharm. J.*, 1913 (4), 37, 876.

<sup>2</sup> *J. Am. Pharm. Assoc.*, 1915, 4, 92.

<sup>3</sup> *J. pharm. chim.*, 1913, 7, 162.

<sup>4</sup> *J. Am. Pharm. Assoc.*, 1912, 411.

<sup>5</sup> *Rep. Pharm.*, 1912, 24, 97.



In this connection attention should be called to the possibility of morphine forming crystalline compounds with sodium or potassium carbonate; hence the use of ammonia as a precipitant is preferable.

Dohme<sup>1</sup> suggests a process of estimating morphine in opium and a number of its preparations which resembles that of Anneler for pantopon (page 502); it depends on retaining the morphine in the aqueous solution, made strongly alkaline with sodium or potassium hydroxide, as an alkali morphinate while the other alkaloids are removed by ether, subsequently making acid and then alkaline with ammonia and extracting the morphine with a chloroform-*isobutyl* alcohol mixture. No analytical results indicating the success of the process were given. Van der Wielen<sup>2</sup> did not find the Anneler process satisfactory on opium.

**Normal Opium.**—The feeling that estimation of morphine alone does not correctly indicate the medicinal value of opium has been growing in recent years, so Van der Wielen (*loc. cit.*) advocates a so-called "normal opium" standardised for its four most important constituents, recommending as a standard the following: morphine, 12%; narcotine, 6%; codeine, 1%; and meconic acid, 5%. He estimates the morphine by some standard lime method (B. P. preferred), the narcotine and codeine by the process given in Vol. VI, p. 393, and the meconic acid colourimetrically as follows:

Macerate 1 gm. of opium with 100 c.c. of water for 24 hours, shaking occasionally; filter, and with 25 c.c. of filtrate, representing 0.25 gm. of opium, mix 5 c.c. of 25% solution of basic lead acetate, let stand at least 15 minutes and filter, washing the precipitate with water till the washings are colourless. Dissolve the precipitate in warm *N*/10 hydrochloric acid making up to exactly 100 c.c., which will give a slightly yellowish solution. As a comparison standard dissolve 0.05 gm. of meconic acid in *N*/10 hydrochloric acid to make exactly 250 c.c. adding sufficient Orange G. to give a colour identical with that of the solution from opium. A colourimetric comparison of the two solutions may now be made, using 1 drop of ferric chloride test solution to 5 c.c. of each solution to produce the characteristic colour with meconic acid, and employing any suitable colourimeter.

**Estimation of Morphine in Compounds.**—The accurate determination of morphine in galenical compounds is often extremely difficult, and while in fluids such as camphorated tincture of opium or even Sydenham's laudanum reasonably good results are obtainable if especial care is used, in a preparation such as the U. S. P. Compound Licorice Mixture, results by any process so far devised are very unreliable even though duplicates may be concordant. The writer is aware that considerable work has been done on the assay of this mixture and that some analysts believe it possible to determine the morphine with fair accuracy, but so far all actual results he has seen do not substantiate this belief.

<sup>1</sup> *J. Amer. Pharm. Asso.*, 1915, 4, 85.

<sup>2</sup> *Yearbook of Pharm.*, 1913, 443.



A process applicable to acid opium liquors and designed especially for Sydenham's laudanum is given by Debourdeaux<sup>1</sup> and involves the following considerations. Morphine is soluble in 100 parts of water saturated with carbon dioxide, but a solution of morphine in lime water precipitates both calcium carbonate and morphine when treated with carbon dioxide. If now a lime water solution from opium, containing the morphine, is treated with the gas the calcium carbonate and morphine are precipitated, but on continued treatment to complete saturation the morphine redissolves.

To 150 c.c. of Sydenham's laudanum add an excess of freshly slaked lime, dilute the mixture with water to 300 c.c. and allow to stand for about half an hour, shaking frequently or continuously; filter and wash the precipitate with 50 c.c. of water. The precipitated magma is now mixed with 150 c.c. of water, the mixture again filtered and the precipitate washed with three 50 c.c. portions of water. The whole mixed filtrate is now saturated with carbon dioxide, filtered if necessary, the precipitate washed with water saturated with the gas, and the filtrate and washings evaporated to 100 c.c., cooled, 50 c.c. of ether and 10 c.c. of *N/1* ammonia added, and after thorough shaking the whole set aside for 24 hours. The precipitated morphine is washed with water saturated with morphine and ether, dried at 100° and then mixed with 5 gm. of slaked lime and 118 c.c. of water. After solution of the crystals, filter and to an aliquot part (preferably 80 c.c., representing 100 c.c. of the original laudanum) add 10% by volume of alcohol, 50% of ether and 2% of ammonium chloride. Let stand 24 hours after thorough shaking, collect the crystals, wash and dry as before, wash again with petroleum ether, dry at 100° and weigh. (Instead of weighing, as recommended, it would be preferable to titrate.) Add the correction for morphine in the mother liquors, as determined by LeClere,<sup>2</sup> of 31 mg. for each 50 c.c. of the final solution used for precipitation.

The estimation of morphine in plain tablets or pills, while not usually difficult, offers some probable complications. If a lime method is used any starch present must be removed by filtering the solution of the tablet and treating the sediment with water and acid before lime is added, otherwise some morphine will be absorbed by the starch in the alkaline solution (see Debourdeaux).<sup>3</sup> Lactose, glucose, gum and dextrin also may interfere. With regard to lactose, see page 505. The best procedure is therefore to use some approved shake-out method, and though a number of these have been described in the literature, for lack of space only one will be fully given here with brief mention of other similar methods, the one selected being essentially that of Williams.<sup>4</sup>

Dissolve a sufficient number of the tablets to give about 0.1 to 0.2 gm. of morphine in a few c.c. of water acidified with hydrochloric acid. If any in-

<sup>1</sup> *J. Pharm. Chim.*, 1913, 8, 424.

<sup>2</sup> *J. Pharm. Chim.*, 1913, 7, 521.

<sup>3</sup> *J. Pharm. Chim.*, 1913, 8, 301.

<sup>4</sup> *Am. J. Pharm.*, 1914, 86, 308.

soluble matter is present, filter and wash the precipitate thoroughly with dilute hydrochloric acid and water and evaporate the filtrate to a volume of about 10 c.c. If the tablets are completely soluble, keep the volume of the solutions to about 10 c.c. Transfer to a separating funnel and add 15 c.c. of a mixture of 2 volumes of chloroform and 1 volume of alcohol and then sufficient 10% ammonia to make distinctly alkaline; agitate carefully and thoroughly for several minutes and draw off the chloroform solution through a pledget of cotton. Repeat this extraction twice more and then use three 10 c.c. portions of chloroform alone. Evaporate the combined chloroform extracts to dryness, add a few drops of alcohol and again evaporate. Dissolve the residue in 10 c.c. of *N*/10 acid and titrate with *N*/50 alkali, using cochineal as indicator.

A similar process, using three extractions with 50 c.c. portions of amyl alcohol, was suggested by Bernegau and Heidelberg in a paper before the Pennsylvania Pharmaceutical Association in 1912 which process was modified by E'we and Vanderkleed.<sup>1</sup> Anneler's method applied to pantopon (see page 502) may also be used to advantage and has been found very useful by Englehardt.<sup>2</sup> Thorburn<sup>3</sup> uses as a solvent 3 volumes of phenylethyl alcohol and 1 volume of benzene.

In tablets containing no diluent except cane or milk sugar, simple solution in water, precipitation with ammonia, and weighing or titration of the washed and dried crystals is quite satisfactory.

Reference may be made to the work of Adams and Doran<sup>4</sup> on smoking opium and its composition, showing variations in morphine from about 8% to 17%.

Pott<sup>5</sup> found that some undecomposed morphine sublimed with opium smoke at atmospheric pressure, this being detected by its action on the respiratory centres of rabbits and by the biological reaction on mice.

**Toxicology of Opium and Morphine.**—Investigation by Rosenbloom<sup>6</sup> of the organs of a cadaver 13 months after burial with marked signs of putrefaction showed no substances giving reactions of morphine or other alkaloids, nor was there evidence of any substances interfering with the usual processes of estimating morphine.

Grutterink and Van Ryn<sup>7</sup> in the course of some investigations found that 2½ years after death it was possible to show definitely the presence of morphine in both the stomach and liver, though only minute quantities were found in the liver. Identification was made by various colour reactions and by actual separation of crystals of morphine. Doepmann<sup>8</sup>, in order to test carefully the stability of morphine and the value of toxicological

<sup>1</sup> *J. Am. Pharm. Assoc.*, 1913, 979.

<sup>2</sup> *Ap. Ztg. (New York)*, 33, 141.

<sup>3</sup> *J. Ind. Eng. Chem.*, 1911, 3, 754.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1912, 4, 429.

<sup>5</sup> *Biochem. Zeit.*, 42, 67.

<sup>6</sup> *J. Biol. Chem.*, 18, 131.

<sup>7</sup> *Pharm. Weekblad.*, 1915, 52, 423.

<sup>8</sup> *Chem. Zeit.*, 1915, 39, 69.

examinations long after putrefaction has set in, mixed varying amounts of morphine hydrochloride with chopped horse flesh and examined the mixture at intervals of from 1 to 11 months. He was able to isolate and obtain characteristic reactions of morphine in every case, even when as little as 20 mgm. had been added to each kilo of flesh and after standing for 11 months.

#### ERRATA IN VOL. VI.

Page 353, line 4, for page 354 read page 407.

Page 365, title, for "sovlents" read "solvents."

Page 389, line 9, for "carbonate" read "bicarbonate."

# STRYCHNOS ALKALOIDS.

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By CHARLES E. VANDERKLEED.

The many species of the genus *Strychnos* have a widely varying physiological action, according as they contain more, less, or in some cases no strychnine or brucine. A. F. Sievers<sup>1</sup> tabulates those species of *Strychnos* which have thus far been reported on as to their content of strychnine and brucine.

The seeds of *Strychnos Nux Vomica* continue to afford the principal source of the alkaloids strychnine and brucine. The Madras and Bombay districts of India, and the Saigon district of Cochin China are the commercial geographic sources of this drug. In none of these districts has the cultivation of the nux vomica tree become a business. The trees grow in a wild state, attaining a height of 30 to 40 ft., and a circumference of 3 to 4 ft. Their growth and development depend largely on the extent of the rainfall in the district to which they are indigenous. The young trees, however, in their wild state are in some cases attended and manured by the natives, and in such cases they come into bearing in 10 to 12 years. When it is desired to cultivate the nux vomica it is customary to plant the young seedlings in large tubs or pots of rich, loose soil, which must be kept well watered. Poor results have thus far been obtained when raised or cultivated as garden or plantation trees. The seeds are harvested from March to July.

**Oil of Nux Vomica.**—In the preparation of extract of nux vomica a small quantity of heavy fixed oil sometimes separates and may be skimmed off. This oil is dark brown in colour and has a specific gravity of about 0.956 at 25°. When subjected to the following assay process, a sample of this oil yielded 4.66 grm. of strychnine per 100 c.c.

Dissolve 10 c.c. of the oil in 40 c.c. of ether and shake out with three portions of 5% sulphuric acid. Make alkaline with ammonia, shake out with chloroform and complete the assay by the U. S. Pharmacopœia method for the assay of the drug.

**Test for Brucine in Strychnine.**—D. B. Dott<sup>2</sup> condemns the use of undiluted nitric acid in testing strychnine for the presence of brucine. He advocates the use of a 1 : 1 nitric acid stating that this will detect 0.01% of brucine in strychnine. He recommends for pharmacopœial use the following test: "When 0.05 grm. of the strychnine in powder form is dissolved at the ordinary temperature in 4 c.c. of acid prepared by mixing equal volumes of nitric acid and water, the colour should, after 5 minutes, be purely yellow, showing

<sup>1</sup> *Midland Druggist and Pharm. Rev.*, 1911, 45, 233.

<sup>2</sup> *Pharm. Jour.*, 89, 144-171.

no red or orange tinge." In using the nitric acid method for the estimation of strychnine in the presence of brucine, Dott employs 1 c.c. of concentrated nitric acid and 10 c.c. of diluted sulphuric acid for every 0.25 gm. of brucine. On standing for 10 minutes at ordinary temperature all brucine is destroyed. If kept at 40°, however, an appreciable amount of strychnine is destroyed.

Species	Synonym or common name	Habitat	Parts used	Constituents (strychnine and brucine)	Uses, remarks, etc.
<i>S. Nuxvomica</i> Linn.	Poison nut, false angostura bark	Tropical India	Seed, bark and stem	Seeds, strychnine 0.25-2 % brucine 0.50-2 % Bark, brucine (anhyd.) 7.78 % Wood, brucine (anhyd.) 2.26 % Leaves, brucine (anhyd.) 0.33 %	Medicinal
<i>S. Ignatii</i> Berg.	St. Ignatius bean	Philippine Islands	Seeds	Strychnine, 0.52-1.5 % Brucine, 1.43 %	Medicinal
<i>S. Colubrina</i> Linn.	Serpent's wood	East Indies	Wood	Wood, 0.96 % total alkal. Bark, 5.54 % total alkal. (Both strychnine and brucine present)	Antidote for snake bites and medicinally.
<i>S. Rheedii</i> Clarke	Serpent's wood	Malabar	Wood and leaves	Wood and bark—strychnine and brucine Seeds, 0.06 % brucine	Antidote for snake bites and medicinally
<i>S. polatorum</i> Linn.	Clearing nut	Ceylon, E. Indies	Seeds	Traces of brucine	Clarifying water, also medicinally
<i>S. guianensis</i> Mart.		Guiana	Bark	Strychnine and brucine	Arrow-poison (curarine, a poisonous alkaloid constitutes the poison). Medicinally
<i>S. Tientae</i> Leschen		Java	Root-bark	Root-bark—strychnine. Leaves and seeds—about 1.4 % strychnine and trace of brucine	Arrow-poison
<i>S. pseudochina</i> St. Hill.		Brazil	Bark	None	Intermittent fever
<i>S. ligustrina</i> Zipp.		Malayan Archipelago	Bark and wood	Bark—7.78 % anhyd. brucine	
<i>S. laurina</i> Wall.			Wood	Leaves, none	
<i>S. monosperma</i> Miq.		Java		None	
<i>S. malaccensis</i> Benth.		Cochin-China	Bark	Brucine	Hydrophobia
<i>S. javanica</i>		Cochin-China	Bark	2.7 % brucine	Hydrophobia
<i>S. suaveolens</i> Gilg.		West Africa	Wood	Brucine	
<i>S. Icafe</i> Baill.		Africa	Wood	Strychnine in bark, leaves and roots	Arrow-poison
<i>S. toxifera</i>		Guiana	Bark	None	Arrow-poison
<i>S. aculeata</i>		Africa	Seeds	Strychnine, none; brucine, about 0.05 % mostly in kernels	Fish-poison (poisonous action due to a glucoside)
<i>S. Ouagha</i> Gilg.		East Africa	Fruits	Seeds—strychnine, none; brucine, trace	Fruit (pulp) used for food
<i>S. spinosa</i> Lam.		East Africa	Fruit	Seeds—trace	Fruit (pulp) used for food
<i>S. Tonga</i> Gilg.		East Africa	Fruit	Seeds—trace	Fruit (pulp) used for food

**The Assay of Nux Vomica and Its Preparations.**—*Method of the United States Pharmacopœia.*—Having concluded that in the hands of many operators the assay of nux vomica and its preparations for strychnine only, by the nitric acid method, is liable to lead to erroneous results, and having also been satisfied that the proportion of strychnine to brucine in nux vomica seeds does not greatly vary, the Revision Committee of the United States Pharmacopœia have chosen for the forthcoming issue (Ninth Revision) a method for total alkaloids, adopting as a standard for the drug not less than 2.5%, for the fluid extract not less than 2.37 nor more than 2.63 gm. total alkaloids in 100 c.c., and for the tincture not less than 0.237 nor more than 0.263 gm. total alkaloids in 100 c.c.

The process for the *drug* consists in extracting by maceration with a mixture of chloroform and ether, with ammonia water to liberate the alkaloids, taking an aliquot part, extracting with diluted sulphuric acid, rendering alkaline with ammonia, extracting with chloroform, evaporating, weighing, and titrating against *N*/10 sulphuric acid, using the average molecular weight of strychnine and brucine as the basis for the calculation. The *fluid extract* is diluted with ammonia water and shaken out, following the same method as used for the drug. 100 c.c. of the *tincture* are evaporated to 10 c.c. and assayed in the same way as the fluid extract.

*Method of the British Pharmacopœia, 1914.*—In the new British Pharmacopœia, 1914, the ferrocyanide method of assay of nux vomica preparations (see Vol. VI, p. 473) of the 1898 edition has given way to the nitric acid method. For the *drug*, the method is essentially as follows:

7.5 gm. of nux vomica in No. 60 powder are macerated with frequent shaking for half an hour with a mixture of 25 c.c. of chloroform, 50 c.c. ether, and 5 c.c. ammonia. 50 c.c. of the clear liquid (representing 5 gm. drug) are transferred to a separator and shaken out with three portions each of 10 c.c. of *N*/1 sulphuric acid solution. The combined acid solutions are rendered alkaline with ammonia and shaken out with three portions of chloroform.

The chloroform is recovered from the combined solutions, and the alkaloidal residue is dissolved in a mixture of 5 c.c. of diluted sulphuric acid and 10 c.c. water. The solution is warmed to 50° and 3 c.c. of a mixture of equal volumes of nitric acid and water are added to oxidise and destroy the brucine. After 10 minutes the solution is made alkaline with solution of sodium hydroxide and shaken out with three portions of chloroform. The mixed chloroform solutions are washed with 5 c.c. of water and evaporated to dryness in a tared dish. 5 c.c. of alcohol are added and evaporated, and the residue of strychnine alkaloid dried at 100° and weighed. The standard for nux vomica is not less than 1.25% of strychnine as determined by the above method.

The *liquid extract* is assayed by taking 10 c.c., evaporating to a syrupy extract, dissolving in 20 c.c. of water, rendering alkaline with a solution

of 5 gramm. sodium carbonate in 25 c.c. water, and shaking out with chloroform, after which the method for the drug is followed as outlined above. The standard for liquid extract of nux vomica is not less than 1.45 gramm. nor more than 1.55 gramm. of strychnine in 100 c.c.

The *dry extract* is assayed by exhausting 3 gramm. with 70% alcohol and testing the alcoholic solution by the process as outlined for the liquid extract. The standard for dry extract of nux vomica is not less than 4.8 gramm. nor more than 5.2 gramm. of strychnine in 100 gramm.

The *tincture* is assayed by the process described under the liquid extract. The standard for tincture of nux vomica is not less than 0.120 gramm. nor more than 0.130 gramm. of strychnine in 100 c.c.



# CINCHONA ALKALOIDS.

By OLIVER CHICK.

**Cinchona Ledgeriana Seeds.**—Previous investigators have failed to find any alkaloids in the seeds of *C. Ledgeriana*, *C. officinalis*, or *C. succirubra*. P. van Leersum<sup>1</sup> however, by the following process of extraction has obtained up to 0.38% of total alkaloids on the dried seeds of *C. Ledgeriana*. The seeds, after powdering, were extracted with petroleum ether to free them from fat, the powder was dried, reground, mixed with slaked lime and sodium hydroxide solution, and extracted with benzene. The mixed alkaloids were extracted from the benzene by hydrochloric acid.

**Cuprea Bark.**—Two parcels of this bark, now seldom seen, offered for sale this year (1914), and examined in Messrs. Howards and Sons' laboratory, were found to contain no cupreine.

**Titration of Cinchona Alkaloids.**—Richter<sup>2</sup> states that the Fifth German Pharmacopœia (1910) method does not give concordant results, and that Poirrier's blue and lacmoid are better indicators to use than hæmatoxylin. He recommends the following acid method of extraction and estimation. 3.75 gm. of powdered bark are warmed on the water-bath with 2.5 c.c. of 25% hydrochloric acid and 20 c.c. of distilled water for 15 minutes. When cold, 30 gm. of chloroform and 60 gm. of ether are added, and the whole shaken. 10 c.c. of 10% sodium hydroxide solution are now added, and the mixture again shaken during 15 minutes. The ethereal layer is then cleared by the addition of 1 gm. of powdered tragacanth and 0.5 gm. of ignited magnesia. The chloroform-ether extract is filtered, and 60 gm. shaken out with 20, 20 and 10 c.c. of *N*/10 hydrochloric acid, and then with 10 c.c. of water. The organic solvents are driven off, and the aqueous portion made up to 250 c.c. 100 c.c. of this are treated with 20 c.c. of water and 30 c.c. of *N*/10 picric acid solution. When the precipitate has settled, 50 c.c. of clear liquid are filtered off and titrated with *N*/10 potassium hydroxide solution, using phenolphthalein as indicator.

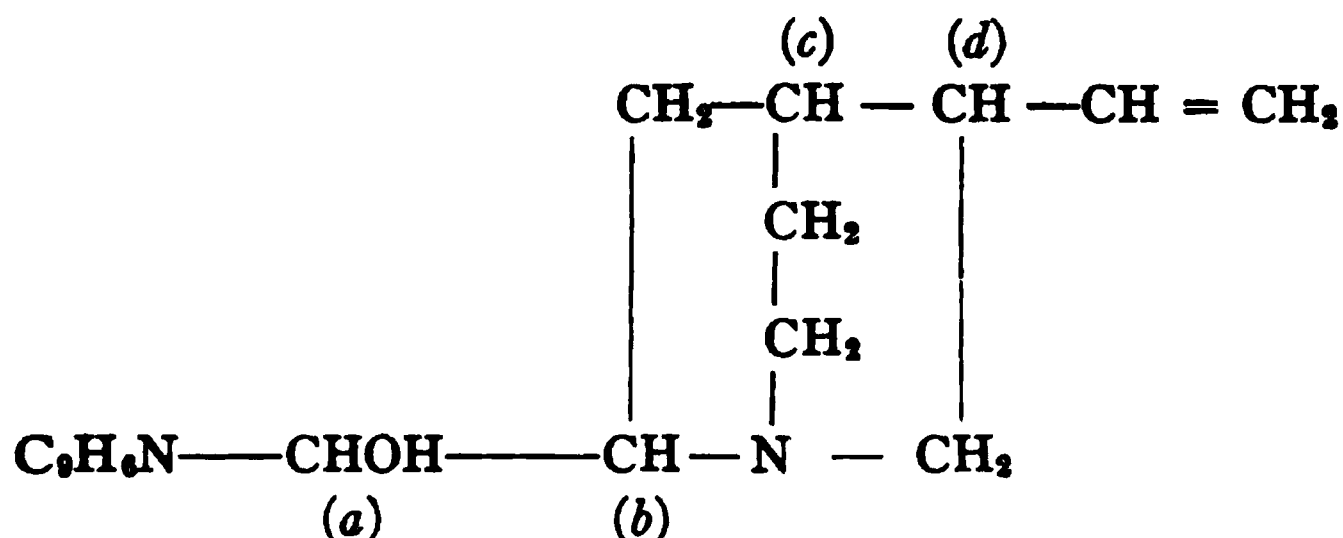
R. Gaze<sup>3</sup> also finds that the method prescribed in the Fifth German Pharmacopœia for the estimation of alkaloids in cinchona barks is unreliable in the case of those of high alkaloidal content, more chloroform-ether mixture and sodium hydroxide solution being required than therein stated; moreover, the temperature of extraction is important as more alkaloid is extracted at 30° than at 15°.

<sup>1</sup> *Pharm. Weekblad.*, 1913, 50, 1464-1467.

<sup>2</sup> *Apoth.-Zeit.*, 1912, 27, 949-950, 960-961.

<sup>3</sup> *Apoth.-Zeit.*, 1913, 28, 144-147.

**Constitution.**—The constitution of the cinchona alkaloids, although not yet known with certainty, is becoming better understood each year, thus enabling chemists to convert certain of these alkaloids into others closely related to them. The isomerism in this group is now known to be due to the spatial arrangement around the asymmetric carbon atom marked (b) in the following formula for cinchonine, since the asymmetry of the other three carbon atoms (a), (c), and (d) may be destroyed without interfering with the isomerism of the products.



Following up the conversion of cinchonine into cinchonine by Rabe,<sup>1</sup> Kaufmann and Huber have converted hydrocinchonine (hydrocinchotoxine) into a mixture, which on careful examination showed the presence of about 50% hydrocinchonine and 10% hydrocinchonidine.<sup>2</sup>

It has been found possible to prepare the hydrocinchona alkaloids in nearly theoretical yield by the hydrogenation of the alkaloids under pressure in the presence of palladium black as catalyst (see page 519). Every other method of hydrogenation invariably splits the second half of the molecule, yielding amorphous gummy bodies which do not give crystalline salts.

Rabe and his pupils<sup>3</sup> have started some preliminary experiments on the synthesis of cinchona alkaloids which may be watched with great interest.

Dobbie and Fox<sup>4</sup> have confirmed the presence of the 6-methoxyquinoline nucleus in quinine, and the 6-hydroxyquinoline nucleus in cupreine by means of their absorption spectra, which are practically identical with the absorption spectra of 6-methoxyquinoline and 6-hydroxyquinoline.

**General Properties of Cinchona Alkaloids.**—G. N. Watson<sup>5</sup> gives the following test for *cinchona alkaloids*. A freshly prepared alcoholic solution of  $\alpha$ -naphthol is treated with a little strong sulphuric acid (2 drops to 1 c.c.). When a few drops of this reagent are added to an aqueous solution of quinine sulphate a yellow precipitate is produced, soluble in excess of the reagent to a yellow solution. Sulphates of quinidine, cinchonine, and cinchonidine, but no other white alkaloids, give this yellow colour, which may be obtained with 1 c.c. of a 1 : 2000 solution of quinine sulphate.

<sup>1</sup> Ber., 1908, 41, 67; 1911, 44, 2088.

<sup>2</sup> Ber., 1913, 46, 2913.

<sup>3</sup> Ber., 1912, 45, 2163.

<sup>4</sup> Trans., 1912, 101, 77-81.

<sup>5</sup> Amer. J. Pharm., 1913, 85, 502.

**Quinine.**—J. Ville<sup>1</sup> states that anhydrous crystals of quinine are easily obtained by blowing air through a wash-bottle containing ammonia into a solution of from 1 to 20% strength of quinine hydrobromide heated on the water-bath. G. L. Schaefer<sup>2</sup> has obtained anhydrous quinine in the form of slender needle-shaped crystals by allowing the gelatinous mass obtained by dissolving quinine hydrate in a small amount of acetone to stand for several days.

**Detection and Estimation of Quinine.**—A new method of applying the thalleioquin test for quinine is given by C. H. LaWall,<sup>3</sup> the following reagent being required: 0.5 gm. of potassium bromate dissolved in 10 c.c. of 10% hydrobromic acid is made up to 100 c.c. 100 c.c. of the quinine solution, which may be as weak as 1:200,000, are placed in a Nessler cylinder and 5–10 drops of the bromine reagent added, when a green tint is obtained. In testing drugs or extracts, about 1 gm. of the material is shaken with ammonia and 20 c.c. of ether, the ether extract being evaporated to dryness. The residue is taken up with 1 c.c. of *N*/10 sulphuric acid, and made up to 15 c.c. with water. 5 c.c. are then placed in a Nessler cylinder, made up to 100 c.c. and tested as above. Should no green tint be obtained the remaining 10 c.c. may be tested similarly. Should no green colour be now produced the cinchona alkaloids which give the thalleioquin reaction (see Vol. VI, p. 507) are absent, or present in amount to less than 0.1 mg.

C. Mannich and L. Schwedes<sup>4</sup> state that pyramidone (1-dimethyl-amino-2:3-dimethylpyrazolone) prevents the thalleioquin reaction, a red colour being obtained instead of a green. Pyramidone also interferes with the herepathite reaction. It may be separated from quinine by shaking out the bases from an alkaline solution, and washing the extract thoroughly with water, the pyramidone being removed in the water.

P. J. Kruysse<sup>5</sup> gives a method for the separation of quinine from other cinchona alkaloids by precipitation as nitroprusside, but gives no indication of the accuracy of the method.

T. Cockburn and J. W. Black<sup>6</sup> have published a method for the estimation of quinine in certain organic liquids, which gives excellent results if the details of manipulation are strictly adhered to. In testing urine, 250 c.c. of the sample are made strongly alkaline with sodium hydroxide, warmed, and extracted three times with ether (at as high a temperature as practicable). The combined ether extracts are washed with water, placed in a flask, the ether evaporated, and the residue dried in the steam-bath. It is dissolved in 20 c.c. of anhydrous ether and the solution filtered into a weighed 4 ounce conical flask, with the ethereal washings of the flask and filter. With the flask is weighed a filtering tube, consisting of a small thistle-funnel with a

<sup>1</sup> *Bull. Soc. Chim.*, 1912, 11, 398.

<sup>2</sup> *8th Int. Cong. Appl. Chem.*, 1912, Sect. VIII B, 75–84.

<sup>3</sup> *Amer. J. Pharm.*, 1912, 84, 484.

<sup>4</sup> *Apoth. Zeit.*, 1912, 27, 343.

<sup>5</sup> *Chem. and Drug.*, 1913, 82, 34.

<sup>6</sup> *Analyst*, 1911, 36, 396.

10-mm. bulb packed with asbestos. To the ethereal solution are added 10 c.c. of saturated ethereal solution of citric acid, and after 24 hours the liquid is filtered through the tube by suction, and the precipitate washed three times with 10 c.c. of ether which is similarly drawn off through the filter tube. Filter and flask are now dried, at first at a low temperature, finally at 100°, and weighed. The process may be used for the estimation of quinine in the presence of caffeine, but not for the separation of quinine from other cinchona alkaloids.

**Salts of Quinine.**—The British Pharmacopœia, 1914, has substituted the Kerner test for the methods of testing quinine salts given in the 1898 edition. In doing so it has raised the standard of purity of these salts from products containing 8 to 9% of other alkaloidal sulphates to products containing about 3% cinchonidine sulphate together with 1 to 2% hydroquinine sulphate (*i.e.*, the normal amount in quinine sulphate).

**Quinine Sulphate.**—The British Pharmacopœia, 1914, has changed Dr. Paul's gravimetric test of the 1898 Pharmacopœia for Prof. Kerner's volumetric test. The details of the test are exactly similar to the British Pharmaceutical Codex test except that the quinine sulphate is dried at 50° (until only two mols. of water of crystallisation remain) before weighing out the 2 gm. of the salt for the test (see Vol. VI, pp. 520–521). 6 c.c. of ammonia, sp. gr. 0.959 are allowed.

**Quinine Hydrochloride.**—The British Pharmacopœia, 1914, gives the following modified Kerner test for quinine hydrochloride. “2 gm. are dissolved in a warm mortar in 20 c.c. of water at 60°, 1 gm. of powdered non-effloresced sodium sulphate added, the mixture triturated, cooled, allowed to stand at exactly 15° for half an hour with occasional stirring, the crystals of quinine sulphate pressed and the expressed liquor filtered. 5 c.c. of this filtrate, transferred to a dry test-tube and brought to a temperature of 15° yield, on the gradual addition of 6 c.c. of solution of ammonia, also at a temperature of 15°, a precipitate which redissolves on rotating the tube.”

It may be noted that the results obtained with samples of quinine hydrochloride by the above test bear no relation whatever to the results obtained by the ordinary Kerner test on samples of quinine sulphate of similar purity (see Vol. VI, p. 528). Moreover, 2 gm. of quinine hydrochloride contain 12% more alkaloid than 2 gm. of quinine sulphate.

N. Tarugi<sup>1</sup> has devised a fairly rapid method for detecting more than 3% of cinchonine and cinchonidine hydrochlorides in quinine hydrochloride. 25 c.c. of the cold quinine hydrochloride solution are saturated with sodium nitrate, allowed to stand for 3 hours, filtered and 5 c.c. of the filtrate treated with 1.5 c.c. of ammonia (sp. gr. 0.880) when should cinchonine or cinchonidine be present to the extent of more than 3% a turbidity is produced.

**Quinine Dihydrochloride.**—The official salt of the 1898 British Pharmacopœia was one having the formula  $C_{20}H_{24}O_2N_2 \cdot 2HCl \cdot 3H_2O$  which should

<sup>1</sup> *Gazzetta*, 1914, 44, I, 131–151.

contain 12% of water; but, as was pointed out in Vol. VI, p. 528, the salt met with in commerce contains only 3 to 5% of water. The 1914 Pharmacopœia recognises this, giving the formula as  $B_2HCl$  and allowing a 3% water-content. It states that 1 grm. of the salt dissolved in 20 c.c. of water requires for neutralisation not more than 5.0 c.c. of normal sodium hydroxide solution with phenolphthaleïn as indicator. The Kerner test is carried out on this salt as for the hydrochloride except that the salt is dissolved in 15 c.c. of water and 5 c.c. of normal sodium hydroxide solution. The same remark applies to this Kerner test as to that for the hydrochloride; and the alkaloid content of the dihydrochloride is half way between that of the sulphate and the hydrochloride.

**Quinine Formate.**—Hampshire and Pratt<sup>1</sup> having examined several commercial samples of quinine formate find that it is a monohydrate of the formula  $C_{20}H_{24}O_2N_2 \cdot HCOOH \cdot H_2O$ , and is not anhydrous as is generally stated.

**Quinine Glycerophosphate.**—Rogier and Fiore<sup>2</sup> describe quinine glycerophosphate  $(C_{20}H_{24}O_2N_2)PO_3 \cdot OC_3H_7O_2 \cdot H_2O$  as white needles becoming somewhat yellow on exposure to light. It melts at  $180^\circ$ – $181^\circ$  and is soluble in 78 parts of boiling water;  $[\alpha]_D^{21} = -133^\circ 33'$  (0.2474 grm. of anhydrous salt in 20 c.c. of 90% alcohol),  $[\alpha]_D^{17} = -140^\circ 24'$  (0.2093 grm. in 20 c.c. of absolute alcohol).

**Citrate of Iron, Quinine, and Strychnine, Easton's Syrup, Etc.**—While the total alkaloids in these preparations may be estimated with ease and accuracy by the ordinary methods, no satisfactory method for the separation of the quinine and strychnine existed before the modification of the ferrocyanide method lately proposed by Simmonds.<sup>3</sup> Excellent results are obtained if the details of the process are adhered to. The strychnine must not exceed 0.1 grm. in the 50 c.c. of acid used; and it has been found in Messrs. Howards and Son's laboratory that not more than 3 hours should be allowed for the ferrocyanide precipitation to prevent excessive co-precipitation of the quinine. Having obtained and weighed the total alkaloids in the usual way (from 5 to 10 c.c. of Easton's syrup, and 5 grm. of citrate of iron, quinine and strychnine are convenient quantities to take), these are dissolved in 50 c.c. of 10% sulphuric acid. 5 c.c. of 4% potassium ferrocyanide solution are run in from a burette drop by drop, stirring well, and the mixture set aside (3 hours). The precipitate is filtered through a small filter (7 cm.) and washed lightly with about 3 c.c. of 5% sulphuric acid. With the aid of about 10 c.c. of 10% ammonia solution and a fine jet of water the precipitate is washed into a small separator and extracted three times with chloroform, using 15, 10 and 5 c.c. The chloroform solutions are collected in another separator, and the alkaloids extracted from them with 50 c.c. of 20% sulphuric acid, using 30, 10, and 10 c.c.; then the precipitation and other operations are repeated as before, until

<sup>1</sup> *Pharm. J.*, Special Issue, 1913, 26.

<sup>2</sup> *Bull. Sci. Pharmacol.*, 1913, 20, 72.

<sup>3</sup> *Analyst*, 1914, 39, 81–83.

the chloroform extracts are again obtained. The chloroform is evaporated carefully, a little alcohol being added towards the end to prevent spluttering, and the residue of strychnine weighed after drying it for an hour or so at 100°. The quinine may be taken by difference between the total alkaloid and strychnine, or by bulking the two acid filtrates, making alkaline, and extracting with chloroform or ether.

**Aristoquinine and Euquinine.**—Aristoquinine is usually called carbonate of quinine. Biginelli,<sup>1</sup> however, regards it as carbonylquinine  $(C_{20}H_{23}O_2N_2)_2 \cdot CO$ , having prepared the true anhydrous carbonate  $B_2H_2CO_3$ , m. p. 168°–169°, by passing carbon dioxide into a solution of quinine in aqueous ether (see Vol. VI, p. 59). Similarly euquinine is the ethyl ester of quinine-carbonic acid, and not ethylcarbonate of quinine. Were these bodies merely salts of quinine, alkalis would liberate the alkaloid from them; this, however, is not the case, even hot alkalis being without action on them. Moreover, they are rapidly hydrolysed by boiling dilute acids, after which treatment the quinine may be recovered by making the solutions alkaline and extracting with ether.

Angeloni<sup>2</sup> gives the solubility of aristoquinine as 0.20% in ether, and of euquinine as 3.33% in ether.

**Hydroquinine.**—In view of the increased demand for hydroquinine sulphate and the difficulty of its economical manufacture from commercial quinine sulphate by the acid sulphate and permanganate method (see Vol. VI, p. 533, footnote), the following new method of preparation by hydrogenation of quinine sulphate is of great importance.

“One part of palladium black is added to a solution of 250 parts of quinine sulphate in 1,400 parts of water and 40 parts of sulphuric acid, and the mixture is shaken with hydrogen under a low pressure until it is stable towards permanganate: after filtration the solution is neutralised whilst hot, when hydroquinine sulphate will at once crystallise in the form of slender needles.”<sup>3</sup>

No methods have been given for testing the purity of hydroquinine sulphate, but the following have been used by the writer. No mineral matter should be left on gentle ignition. No ammonium salts should be indicated on boiling a little of the cold water washings of the salt with sodium hydroxide. 1 grm. of the salt dissolved in 20 c.c. of dilute sulphuric acid and cooled to 0° by means of ice, should not immediately discharge the colour from 1 drop of 1% permanganate solution (test for non-hydrogenated alkaloids). The alkaloid obtained by passing through ether and ammonia and taking to dryness should dissolve almost completely in a little chloroform (test for hydrocinchonidine). The optical rotation may also be taken (Vol. VI, p. 500).

The author has estimated the hydroquinine content of many samples of

<sup>1</sup> *Annali. Chim. Appl.*, 1914, 1, 397–400.

<sup>2</sup> *Boll. Chim. Farm.*, 1913, 52, 675.

<sup>3</sup> *Eng. Pat.* 3948, Feb. 16, 1912.



quinine sulphate from different sources this year (1914), and has found in all cases from 1 to 2%.

**Cinchonine.**—It has been found in Messrs. Howard and Son's laboratories that many commercial samples of cinchonine hydrochloride contain from 2 to 4% of sodium chloride. This impurity is probably due to the method of preparation, as it is found that salt crystallises persistently with cinchonine hydrochloride. Any sodium chloride present may be detected by dissolving some of the cinchonine hydrochloride in chloroform, the inorganic salt being insoluble. To estimate this impurity it is best to incinerate a weighed quantity of the substance at as low a temperature as possible, wash out the sodium chloride from the thoroughly charred mass on a filter, and estimate the chloride in the filtrate by means of silver nitrate.

#### ERRATA. CINCHONA ALKALOIDS, VOL. VI.

Page 494, line 25, for "page 592," read "page 492."

Page 494, line 28, for "page 493," read "page 490."

Page 497, line 33, for "Parrier's blue as indicated," read "Poirrier's blue as indicator."

Page 499, line 17, for "conguinamine," read "conquinamine."

Page 517, line 7, for " $c = 22$ ," read " $c = 2.2$ ."

Page 533, line 17, for "page 199," read "page 512."

Page 535, line 9, for "page 194," read "page 500."

Page 535, line 22, for "tolerabl," read "tolerably."

Page 536, line 27, for "quinine," read "quinidine."

Page 542, line 4, for "pages 520 and 521," read "pages 522 and 525."



# BERBERINE AND ITS ASSOCIATES.

BY EDWARD HORTON.

**Berberine**,  $C_{20}H_{17}O_4N, H_2O$ ; or  $C_{18}H_{11}(OCH_3)_2O_2N, H_2O$ .

Since the publication of Vol. VI, berberine has been synthesised by Pictet and Gams,<sup>1</sup> and converted into hydrastinine by Freund.<sup>2</sup>

**Reactions and Detection.**—Rosenthaler and Görner<sup>3</sup> state that a characteristic behaviour of berberine is that its solutions gelatinise when treated with dinitro- $\alpha$ -naphtholsulphonic acid.

Senft<sup>4</sup> has described a method of detecting hydrastine and berberine microscopically in the seeds of *Hydrastis canadensis*. The powdered endosperms are extracted with ether which removes the fat and the hydrastine. The ethereal extract is evaporated and the residue extracted with alcohol, which dissolves the alkaloid. After filtering and concentrating the alcoholic solution, it is treated with excess of iodine solution, when a coarse-grained black precipitate is formed, which after some time is transformed into small rosette-like groups of crystals. The endosperm after treatment with ether is extracted with hot alcohol which dissolves the berberine. The evaporated filtrate gives all the reactions for berberine described by Tunmann (*Beiträge zur Mikrochemie einiger Wurzelrogen, Gehes Handelsberichte*, 1912). That with zinc chloriodide solution is very characteristic. If some of this reagent is allowed to flow under the cover-glass so as to mix with an aqueous berberine solution, an immediate cloudiness is formed, small crystalline flocks rapidly separate which quickly grow into dense rosettes of extraordinarily thin needles. Side by side with these, single needles and sheaves of needles are observed.

**Estimation: Gravimetric Method.**—Richter<sup>5</sup> recommends the following method: The alcoholic extract of Berberis bark representing 4 gm. of the drug, or an equivalent amount of the tincture, is evaporated to dryness, the residue dissolved in water and 10 c.c. of 15% sodium hydroxide solution added. The whole is shaken with 80 gm. of ether for 10 to 15 minutes and 1 gm. of powdered tragacanth added. 40 gm. of the ethereal solution are treated with 40 gm. of *N*/10 solution of picrolonic acid (nitrophenylmethylisonitrosopyrazolone) and the precipitate of berberine picrolonate collected on a Gooch crucible, washed with a little ether and alcohol, dried at 110° and weighed.

<sup>1</sup> *Compt. rend.*, 1911, 153, 386; *Ber.*, 1911, 44, 2480.

<sup>2</sup> *Annalen*, 1913, 397, 30.

<sup>3</sup> *Zeitsch. anal. Chem.*, 1910, 49, 340.

<sup>4</sup> *Pharm. Post.*, 1913, 46, 977.

<sup>5</sup> *Arch. Pharm.*, 1914, 252, 192.

The weight obtained multiplied by 0.561 gives the equivalent amount of berberine.

David<sup>1</sup> has proposed a new method for the estimation of berberine in hydrastine extracts. The berberine and hydrastine are precipitated with potassium bismuth iodide, and the hydrastine separated by extraction with ethyl acetate. The precipitate is then treated with 10% sodium hydroxide solution and the berberine extracted with a mixture of equal parts of ether and chloroform.

**Hydrastine**,  $C_{21}H_{21}O_6N$ ; or  $C_{19}H_{15}(OCH_3)_2O_2N$ .

**Reactions and Detection.**—Baroni and Borlinetto,<sup>2</sup> who have studied a reaction of calomel with some alkaloids, state that when equal parts of hydrastine hydrochloride and mercurous chloride are triturated together in the presence of water a yellow colouration is immediately produced. A similar behaviour is shown by quinine dihydrochloride, but in this case a brown colour results. Senft's method of detecting hydrastine microscopically is described under Berberine (page 521).

Mayrhofer<sup>3</sup> recommends picrolonic acid as a suitable reagent for the microchemical detection of hydrastine and berberine in plants. The plant section is treated with a mixture of 2 parts of saturated picrolonic acid solution 1 part of glycerol and 1 part of alcohol. At a dilution of 1 in 30,000 berberine sulphate gives crystals in the form of bright yellow clusters, which become brown or black when treated with iodine tincture mixed with an equal volume of glycerol. At a dilution of 1 in 15,000 hydrastine hydrochloride forms crystals, mostly bright yellow in colour, but the smallest may be colourless. They are not altered by treatment with iodine.

**Estimation: Gravimetric Methods.**—The British Pharmacopœia, 1914, gives the following process of estimating hydrastine in Liquid Extract of Hydrastis.

"Transfer 10 c.c. of the liquid extract to a 100 c.c. graduated flask, add 20 c.c. of a solution of potassium iodide diluted with 60 c.c. of water, and then sufficient water to produce 100 c.c. Shake the mixture for several minutes and filter. Transfer 50 c.c. of the filtrate to a separator, render alkaline with solution of ammonia, add 30 c.c. of ether and shake at intervals during several minutes. Allow the liquids to separate, draw off the aqueous portion into a beaker and the ethereal portion into a tared beaker. Return the aqueous solution to the separator, and repeat the operation with two successive portions, each of 20 c.c., of ether for 1 minute. Draw off and reject the aqueous layer; transfer the ethereal solutions to the tared beaker and evaporate at a gentle heat; dry the residue on a water-bath and weigh. The weight is that of the hydrastine in 5 c.c. of the liquid extract examined.

"Examined by the foregoing process liquid extract of hydrastis is found to contain in 100 c.c. 2 gramm. of hydrastine. Limit of error 0.1 gramm. in excess or defect."

The method for the estimation of hydrastine in fluid extracts described in the Dutch Pharmacopœia (4th Edition) is inaccurate in some respects accord-

<sup>1</sup> *Pharm. Post.*, 1915, 48, 1.

<sup>2</sup> *Giorn. Farm. Chim.*, 1911, 60, 241.

<sup>3</sup> *Pharm. Post.*, 1914, 47, 547.

ing to van der Haar,<sup>1</sup> who recommends the following process: 10 gm. of the extract are boiled in a large flask with 20 c.c. of water until the weight is reduced to 10–11 gm: 1.5 c.c. of hydrochloric acid are added, and, after cooling, water is added sufficient to make the total weight up to 20 gm. After shaking with 1 gm. of powdered talc the whole is filtered. 10 c.c. of the filtrate are shaken for 1 minute in a 100 c.c. flask with 4 c.c. of ammonia and 25 c.c. of ether, 25 c.c. of light petroleum and 1.5 gm. of powdered tragacanth are then added, and the whole is vigorously shaken until the liquid becomes clear. 40 c.c. of the ethereal layer are transferred to a flask, another 5 c.c. of light petroleum added, and distilled until 35 c.c. have passed over. The flask is then kept in a cool place for 18 to 24 hours, and after pouring off the mother liquor and washing the crystals with 2 c.c. of light petroleum, these are dried on a water-bath and weighed.

The Fifth German Pharmacopœia<sup>2</sup> describes the following processes for the assay of *Hydrastis* drugs.

**Hydrastis Rhizome** (not formerly standardised).—This is extracted with ether and ammonia for 3 hours, and an aliquot part of the ethereal solution filtered off. The ether is distilled from the filtrate, the solid residue taken up with dilute acid, the solution filtered and the filter washed with water. The acid liquid is then made alkaline with ammonia and the alkaloid shaken out with ether—once only; an aliquot part of the ethereal solution is evaporated and the residue weighed. This is the only case (besides the fluid extract of the same drug) where the alkaloid is weighed and not titrated, and nearly every stage of the process shows a departure from the usual procedure. The requirement is that the alkaloid so obtained shall correspond with 2.5% in the drug, but the amount actually present is probably greater than this, having regard to the final shaking out of the alkaloid with only one portion of ether.

**Fluid Extract of Hydrastis.**—This is diluted with water and then evaporated to remove all alcohol, acidified with hydrochloric acid, the liquid well shaken with talc and filtered. An aliquot part of the filtrate is made alkaline with ammonia and shaken with ether for some minutes, light petroleum is then added and the shaking repeated. After addition of a considerable amount of powdered tragacanth the liquid is further shaken until the ethereal layer is clear. An aliquot part of the latter is filtered off, evaporated and the alkaloid weighed. The amount found is required to correspond with 2.2% in the fluid extract, which therefore does not quite correspond with the rhizome in strength. In this case an intermediate stage of purifying the alkaloid by shaking into acid and back again, has been omitted, being presumably rendered superfluous by the use of acid in the first place, which, with the addition of talc and filtering, is new. The use of tragacanth in separating the ether-petroleum layer is also new, and the latter contains a much larger proportion of light petroleum. The strength is somewhat increased, being formerly 2%.

<sup>1</sup> *Pharm. Weekblad.*, 1911, 329.

<sup>2</sup> *Pharm. J.*, 1911, 86, 295.

Rupp<sup>1</sup> describes a method similar to that of the German Pharmacopœia. Gsell's method<sup>2</sup> of estimating hydrastine and berberine in hydrastis extract depends on the determination of the amount of methoxyl in the respective alkaloids.

David<sup>3</sup> states that for the estimation of hydrastine the methods given in the German and Belgian Pharmacopœias are the most trustworthy, then follows that of the Austrian Pharmacopœia, whilst the French, Dutch, Swiss, and U. S. A. methods are untrustworthy, as the hydrastine obtained by their use is very impure. The U. S. A. method may be improved by removing the alcohol before the hydrastine is extracted with ether. In the estimation of hydrastine, alcohol must be removed previously, berberine should be separated by precipitation with potassium iodide or hydrochloric acid, and the ethereal extract must be mixed with light petroleum, and the mixed solution treated with tragacanth.

### Hydrastinine, $C_{11}H_{13}O_3N$ .

**Reactions.**—Reichard<sup>4</sup> gives a large number of reactions for hydrastinine. The two following are the most characteristic and establish the identity of the alkaloid. A few particles of the hydrochloride are triturated with a minute crystal of potassium ferro- or ferricyanide and a drop of water is then added. With ferricyanide a splendid reddish-green precipitate is obtained, which is characterised by its dichroism. The crystals form elongated prisms and are beautifully developed. When held up to the light they appear bluish dark green with total reflection of the light; the colours are permanent. With the ferrocyanide, crystals are obtained resembling mother of pearl; these are particularly characteristic. Sodium nitroprusside gives a compound not unlike that obtained with the ferricyanide. The behaviour of the alkaloid with sulphuric acid is also noteworthy as the yellow colour produced on warming disappears on cooling, and the test may be repeated over and over again.

<sup>1</sup> *Apoth. Zeit.*, 1909, 24, 922.

<sup>2</sup> *Chem. Zeit.*, 1914, 38, 541.

<sup>3</sup> *Pharm. Post.*, 1915, 48, 1.

<sup>4</sup> *Pharm. Zentr.-h.*, 1911, 52, 1253.

# CAFFEINE, TEA AND COFFEE.

By J. J. FOX AND P. J. SAGEMAN.

Very little additional information concerning the various xanthine derivatives or the constituents of tea and coffee has been published since the article in Vol. VI went to the press. As was perhaps to be expected, most of the new work concerns the methods of analysis, and the usual number of "new" methods for the estimation of caffeine has appeared. We have taken advantage of this opportunity to draw attention to the difficulties which, in our opinion, attend the estimation of caffeine.

There appears to be a useful field for work in the investigation of the constituents of tea and coffee. Much of the best information available rests upon data obtained many years ago and has not hitherto been revised.

**Purine Bases.**—*Identification of purine derivatives by microchemical methods.*<sup>1</sup> Mercuric chloride reacts with those purine bases which contain at least 1 methyl group forming characteristic precipitates. Caffeine and theophylline give rosettes of crystals, while with theobromine smaller masses of crystals result. According to Wagenaar so small a quantity as 1  $\mu$  of caffeine can be detected by breathing on the dried precipitate. Antipyrine-caffeine (*migraine*) does not give the reaction.

According to Camilla and Pertusi<sup>2</sup> xanthine bases may be readily detected in the following manner. The extracted basic compounds are treated with a few drops of concentrated potassium hydroxide solution. A saturated solution of potassium permanganate is then added drop by drop and the mixture warmed. In the presence of xanthine bases gas is evolved. An odour of carbylamine is also said to be observed. (It is, however, difficult to see how carbylamine could be formed in such a case. The only odour detected by the writers was that of methylamine, a normal product of the oxidation of caffeine).

Many new pharmaceutical preparations of purine bases have been prepared recently. A neutral compound of caffeine with aminoacidylphenetidine is stated to be suitable for subcutaneous injections. It is, however, readily split into its components by alkalis. Acidyl compounds of theobromine with stronger acidic properties than the alkaloid are obtained by treatment of metallic salts of theobromine with acid haloids.

C. O. Johns<sup>3</sup> has prepared isomers of theobromine and caffeine by alky-

<sup>1</sup> Wagenaar, *Chem. Zentralb.*, 1914, 1, 1026.

<sup>2</sup> *Chem. Zentralb.*, 1912, 2, 1581.

<sup>3</sup> *J. Biol. Chem.*, 1914, 17, 1.

lating with dimethylsulphate. 2 : 8-Dihydroxy-1 : 9-dimethylpurine yields 2 : 8-dihydroxy-1 : 7 : 9-trimethylpurine, melting at 240°. It is more soluble in water than caffeine and does not give the colouration with chlorine water and ammonia characteristic of the latter substance. 2 : 8-Dihydroxy-1-methyl purine similarly gives 2 : 8-dihydroxy-1 : 7-dimethylpurine. This, on further methylation produces the above-mentioned isomer of caffeine.

**Assay of Caffeine Sodium Salicylate.**—The following method is taken from the British Pharmaceutical Codex. 1 gm. of the drug is dissolved in 20 to 25 c.c. of water and sufficient aqueous sodium hydroxide is added to make the solution alkaline. The liquid is then thoroughly shaken 3 times with chloroform, using successively 15, 10, and 10 c.c. The chloroform solution is evaporated to dryness and the caffeine is weighed. Caffeine sodium salicylate should contain at least 40% of caffeine. Lehmann and Müller<sup>1</sup> recommend the addition of powdered gum tragacanth to the alkaline solution in order to ensure the complete extraction of the caffeine.

**Estimation of Caffeine in Tea, Coffee, Etc.**—From the fact that several investigators have thought it necessary to reexamine the processes for the estimation of caffeine in natural products, it would appear that in many cases difficulty has been experienced in applying the methods described in the literature on the subject. It has already been indicated (Vol. VI, pp. 590-591, 606 and 612) that it is necessary to employ some preliminary treatment in order to decompose those compounds (such as caffeine-potassium chlorogenate) in which the caffeine occurs naturally, before the alkaloid can be completely extracted.

In the case of tea, boiling with water is as a rule sufficient to extract the alkaloid, but with coffee, kola, etc., acid or alkaline treatment is generally necessary in order to ensure the complete liberation of the base. It is apparent that the preliminary treatment should be of such a nature as to leave the material in a condition that will permit of ready permeation by a solvent suitable for the extraction of the caffeine. In our opinion, disregard of this point is frequently responsible for the difficulties that seem to beset the estimation of caffeine. It is not easy otherwise to explain the divergent results obtained by various workers who have used processes which appear to differ only in minor details. In most cases it is probable that the preliminary treatment is sufficient to decompose the caffeine compounds and apparently the failure to extract the caffeine completely is due either to the unsuitable condition in which the material is left for extraction or to the choice of unsuitable solvents. Murray<sup>2</sup> compares Gorter's process<sup>3</sup> with that of Lendrich and Nottbohm.<sup>4</sup> In the former process 11 gm. of the coffee are moistened with 3 c.c. of water, allowed to stand for 30 minutes and then extracted with chloroform for 3 hours; in the latter 20 gm. of coffee are treated with 10 c.c.

<sup>1</sup> *Apoth. Zeit.*, 1911, 26, 647.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1913, 5, 668.

<sup>3</sup> *Annalen*, 1908, 358, 327.

<sup>4</sup> *Zeit. Nahr. Genussm.*, 1909, 17, 241.



of water for 2 hours and then extracted with carbon tetrachloride for 3 hours. The subsequent purification of the extract was of such a nature as to lead to no appreciable loss of caffeine in either case. Murray, however, found that Gorter's method gave much higher results than that of Lendrich and Nottbohm.

As regards coffee we have found that Katz's method, as described on page 609, Vol. VI, gives concordant and accurate results. We prefer the extraction by continuous agitation of the treated coffee with chloroform to extraction in a Soxhlet apparatus, as there is then no doubt that the chloroform is in intimate contact with every part of the finely ground coffee. All workers know the difficulties which arise in extracting a compact moist mass with an immiscible solvent.

Zöller<sup>1</sup> pointed out that caffeine is not affected when heated at 100° with concentrated sulphuric acid, and suggested a method for the estimation of caffeine in tea, involving a preliminary heating at 100° with sulphuric acid. Allen made numerous experiments in order to devise a satisfactory method based on Zöller's principle, but in his experience the process had the objection that caffeine is retained by the charred mass and very prolonged and repeated extractions were necessary to ensure the complete removal of the caffeine.

Costes<sup>2</sup> has recently applied the same principle to the extraction of caffeine in coffee. He recommends the following procedure: 20 grm. of ground coffee are mixed with 15 to 20 c.c. of sulphuric acid (D. 1.835) and heated on the water-bath for 10 to 15 minutes, after which the mixture is extracted with 3 successive quantities of boiling water (200, 150, and 100 c.c.) boiling for 10 minutes after each addition of water. The acid extract is filtered into a basin containing sodium hydroxide solution insufficient in quantity to neutralise all the acid. The solution is made alkaline with sodium carbonate, rapidly evaporated to 250 c.c. and extracted 3 times with chloroform, using successively 50, 35, and 30 c.c. The chloroform extract is evaporated to about 4 c.c., mixed with 2 c.c. of sulphuric acid and heated for 10 minutes on the water-bath. The residue is dissolved in water, filtered, made ammoniacal, cooled and extracted with chloroform. The chloroform is distilled off and the residue weighed. It usually contains not more than 93% of pure caffeine and it is therefore desirable to estimate the nitrogen by Kjeldahl's method and calculate the nitrogen as caffeine. This method is claimed to be especially suitable for caffeine-freed coffee.

In whatever manner the caffeine may have been extracted from coffee, tea or kola it is desirable to make certain that the final extract as weighed is pure caffeine. The most satisfactory check is the determination of the nitrogen by Kjeldahl's method in the weighed residue. Where time is an important factor the caffeine as first extracted may be purified in the following manner suggested by Lendrich and Nottbohm (*loc. cit.*): The residue is treated at

<sup>1</sup> *Zeit. Anal. Chem.*, 12, 106.

<sup>2</sup> *Anal. Chim. Anal.*, 1912, 17, 246.



the ordinary temperature with 10 to 30 c.c. of 1% potassium permanganate. After 15 minutes the excess of permanganate is decomposed by adding, drop by drop, a 3% hydrogen peroxide solution containing 1% of acetic acid. The liquid is then heated on a water-bath for 15 minutes, cooled, filtered, and washed thoroughly. The caffeine is extracted from the filtrate by chloroform in the usual manner.

**Toxicity of Caffeine.**—W. Salant and J. B. Rieger<sup>1</sup> describe the results of a large number of experiments on rabbits, guinea-pigs, cats and dogs. They found the fatal dose to range from 0.14 to 0.35 gm. of caffeine per kilogram of body weight, varying with the mode of administration. Cats and dogs were more susceptible than rabbits or guinea-pigs. Caffeine is not cumulative in dogs and rabbits.

### Tea.

Sawamura's recent investigations<sup>2</sup> led to the following important conclusions as to tea:<sup>3</sup>

(1) In steaming tea leaves it is desirable to limit the steaming so that only the oxidising enzymes are destroyed. This may be effected by steaming for 30 seconds only. The remaining enzymes play an important part in the first stage of rolling tea leaves and it is probable that the production of a fine aroma is dependent on their action.

(2) Green tea is improved in quality by 1 hour's firing at 70°, a higher temperature spoiling the flavour and colour.

(3) The optimum temperature for black tea is 80°.

(4) Refiring is accompanied by a decrease in both the caffeine and tannin.

(5) The operation of rolling crushes the cells and the liberated juices dry on the surface of the leaves. As a consequence, the proportion of readily soluble constituents of the tea is increased.

In view of the widespread opinion that the ratio of caffeine to tannin is an important factor in the valuation of various classes of tea it is interesting to note the patent which has recently been taken out for the adjustment of the ratio between these two constituents by the addition of one or other to tea. It is proposed to make the addition of the necessary constituent by atomising a solution of the substance into the air currents during the drying process (English patent, 10,471, May 2, 1912).

**Moisture in Tea.**—For ordinary purposes the estimation of moisture by heating at 100°–105° under atmospheric pressure gives sufficiently accurate results. In order, however, to avoid inaccuracy due to oxidation, etc., it is preferable to use some method of drying in an inert atmosphere or at reduced pressure. This may be secured either by standing the material in a vacuum desiccator over concentrated sulphuric acid at a pressure of 15

<sup>1</sup> U. S. Dept. Agric., Bureau of Chem., Bull. 148.

<sup>2</sup> Inter. Cong. Appl. Chem., 1912, 18, 313.

<sup>3</sup> For recent work on "The Fermentation of Tea" and the effect of treatment on the quality of the leaf, see Mann, *Reports to the Indian Tea Association, Calcutta*.

mm. for a long period, or alternatively, by heating at  $98^{\circ}$  *in vacuo*. The A. O. A. C. recommend either drying in a current of hydrogen or *in vacuo* for approximately 5 hours in a water-oven.

The use of calcium carbide in estimating moisture has been proposed by F. H. Campbell.<sup>1</sup> The carbide is mixed with a weighed quantity of the sample in a special apparatus and the loss of weight calculated to water, using a factor obtained by treating a portion of the same carbide with a known weight of water. In nearly all cases this method gave higher results than drying either in air or by heating under reduced pressure.

**Tannin in Tea.**—H. L. Smith<sup>2</sup> has worked out a method for the estimation of tannin in tea which is a modification of Chapman's cinchonidine method for the estimation of tannin in hops. It depends upon the complete precipitation of tannin by a saturated solution of cinchonine sulphate, the cinchonine tannate being weighed. A similar method involving the use of quinine was described by Tatlock and Thomson. This method is dealt with in Vol. VI, p. 619. Smith's method is briefly as follows: 10 grm. of tea are boiled with 800 c.c. of water for half an hour, filtered and washed with 200 c.c. of water. The filtrate is cooled and made up to 1,000 c.c. Of this solution 50 c.c. are treated with chloroform to remove the caffeine, and the aqueous liquid is concentrated to about one-third its bulk. 50 c.c. of saturated cinchonine sulphate solution are added to the hot liquid which is then put aside for some hours. The precipitated cinchonine tannate is filtered on a Gooch crucible which has previously been washed with half saturated cinchonine sulphate solution and dried at  $100^{\circ}$ . The precipitate is also washed with half saturated cinchonine sulphate solution and thoroughly dried by suction. The crucible is dried in a vacuum desiccator over sulphuric acid and then heated at  $100^{\circ}$  till constant in weight. This preliminary drying is necessary in order to avoid fusion of the precipitate. The dried precipitate contains 55% of tannin. The method gives results higher than those given by Procter's modification of Löwenthal's method. We have already indicated (Vol. VI, p. 615) that this is due to imperfect knowledge of the nature of the tannin in tea. The results obtained by gravimetric methods for its estimation show that the adoption of an arbitrary factor for the permanganate solution on the assumption that the tannin in tea is gallo-tannic acid is in general inaccurate.

Smith points out the necessity of removing caffeine before precipitation of the tannin, owing to the co-precipitation of caffeine with cinchonine tannate and the impossibility of removing the caffeine from the precipitate by washing.

**Detection of Added Colouring Matter in Tea.**—In view of the prohibition of the entry into the United States of America of artificially coloured teas E. Alberta Read<sup>3</sup> has described the following simple tests for the detection of

<sup>1</sup> *J. Soc. Chem. Ind.*, 1913, 32, 67.

<sup>2</sup> *Analyst*, 1913, 38, 312.

<sup>3</sup> *8th Int. Cong. App. Chem.*, 1912, 18, 301.

added colour. The method allows of the handling of a large number of samples in a short time, thus avoiding undue delay at the place of import. 20 to 25 gm. of tea are placed on a sieve of 16 to 24 meshes to the cm., crushed slightly and then shaken over a piece of white paper. The dust on the paper is crushed by means of a spatula. This procedure streaks the paper and the added colour can be detected, especially with the aid of a lens. Good light is essential for this work.

The usual chemical tests for Prussian blue, indigo, ultramarine and turmeric can be applied. Carbon (graphite) is readily identified by its appearance under the microscope.

As regards Prussian blue, West<sup>1</sup> suggests pressing the powdered tea between sheets of filter paper moistened with oxalic acid solution. On drying the paper and brushing off the tea, blue spots indicate Prussian blue. The natural colouring matter of tea does not stain the paper.

### Coffee.

The question of the aroma of roasted coffee has received renewed attention by Bertrand and Weisweiler.<sup>2</sup> 5 kilos of freshly roasted ground coffee were distilled in a current of steam and the aqueous distillate concentrated to 20 c.c., which contained the whole of the volatile constituents. These 20 c.c. consisted of a heavy oil and an aqueous layer. The aqueous layer was neutralised with hydrochloric acid, filtered and treated with barium silicotungstate. The resulting precipitate was recrystallised from water and dried. It was found to consist of pyridine silicotungstate. 200 to 250 mg. of pyridine per kilo were yielded by various samples of commercial roasted coffee. Pyridine, according to Bertrand and Weisweiler, is an essential factor in the production of the aroma of coffee. If the volatile oil be added alone to sweetened water the characteristic aroma of coffee is not produced unless a corresponding quantity of pyridine is also added.

**Moisture in Coffee.**—The standard method of the A. O. A. C. as described under tea is the most satisfactory for accurate work.

A recent prosecution in England raised an interesting point in connection with the limits of moisture permissible in coffee and chicory mixtures. Hodgson<sup>3</sup> is of opinion that 6% of moisture is too low a maximum limit having regard to the hygroscopic character of ground coffee and chicory mixtures. To test the point Hodgson placed samples of chicory, coffee, and a mixture of chicory and coffee in a drawer and determined the moisture at intervals. He found that in 21 days the increase in moisture was for coffee from 2.0 to 9.7, chicory from 11.3 to 15.9, and for a mixture of chicory and coffee (66% of coffee) from 3.5 to 11.5%. The conditions were described as "similar to those under which coffee and chicory are usually kept in retail shops," but it is very doubtful whether coffee mixtures are generally kept in this manner.

<sup>1</sup> *J. Ind. Eng. Chem.*, 1912, 4, 528.

<sup>2</sup> *Compt. Rend.*, 1913, 157, 212.

<sup>3</sup> *Analyst*, 1913, 38, 454.

**Chlorogenic Acid.**—Gorter<sup>1</sup> describes a delicate and characteristic reaction for chlorogenic acid in coffee and other plants. The substance is boiled with dilute hydrochloric acid for 1 hour, and extracted with ether. The washed extract is concentrated and a dilute solution of ferric chloride is added. A violet colour indicates chlorogenic acid. By this means Gorter has demonstrated the presence of chlorogenic acid in *Ficus Elastica* and *Castilloa Elastica*.

**Caffeol.**—Grafe<sup>2</sup> examined 3 kinds of coffee in order to trace the source of the caffeol: (1) ordinary coffee; (2) caffeine-free coffee which was prepared by treatment with superheated steam followed by benzene; and (3) coffee purified by scrubbing in warm water. No. (2) yielded much less caffeol and also much less crude fibre than Nos. (1) and (3). Grafe concludes that the caffeol has its origin in the crude fibre, the amount of which in (2) was much diminished by the treatment to which it has been subjected.

**Toxic Substances in Coffee.**—Certain acidic constituents of coffee are reputed to have a toxic effect and according to several recent patents these may be removed by roasting the berries with clay or kaolin, preferably with the addition of magnesia. The exact value of treating coffee in this manner is not clear to the authors.

**Caffeine-free Coffee.**—Numerous patents have recently been taken out for removing the greater part of the caffeine from coffee. The most interesting of these depends on the low solubility of caffeine in very cold water. The beans in this case are first extracted with very cold water to remove extractives other than the xanthine alkaloids; the latter are then extracted with hot water. The beans are then made to re-absorb the previously concentrated cold water extract, dried, and roasted.

**Coffee Substitutes.**—In addition to the substances already enumerated in Vol. VI, p. 670, special attention has lately been called to the use of the seeds of *Lathyrus sativus* (a genus of leguminosæ) largely grown in Southern Europe and known as Gesse or Jarosse. Patents have been granted for the use of Soja beans (French patent) and for grains such as rye roasted with juniper berries (English patent). The detection of these materials in admixture with roasted coffee may be readily effected by the aid of the microscope.

The estimation of cereal substitutes in coffee by means of the alkalinity of the ash is recommended by Rozsenyi.<sup>3</sup> He found that the acid required to neutralise the ash of 5 samples of coffee from different sources closely averaged 50 c.c. of *N*/1 acid per 100 grm. of roasted coffee. The ash from 100 grm. of roasted barley, wheat, or rye required about 1 c.c. of *N*/1 acid. These figures form the basis for the calculation of the proportion of coffee in mixtures of coffee with roasted cereals. The examples given by Rozsenyi of the analysis of made up mixtures of coffee and roasted cereals show close agreement with the quantities actually present. These values for the alkalinity of the ash agree with those which we have nearly always found for coffee. In fact

<sup>1</sup> *Rec. Trav. Chim.*, 1912, 31, 281.

<sup>2</sup> *Monatsh.*, 1912, 33, 1389.

<sup>3</sup> *Chem. Zeit.*, 1913, 37, 1482.

we have always considered this determination a valuable one when judging the purity of a sample. Rozsenyi's method forms a valuable adjunct to the microscopical examination, decoction value, etc., of mixtures of coffee with roasted cereals. He also points out that unground roasted coffee may be extracted with water for the preparation of coffee extract, and the exhausted beans dried, glazed and sold as fresh coffee. By this treatment, however, the coffee loses 40% of its mineral matter and the adulteration may be detected by the abnormally low ash of the sample.

**Detection of Chicory Extract in Decoctions of Coffee and Chicory.**—LaWall and Forman<sup>1</sup> recommend a determination of the cupric reducing power as a means of detecting the presence of chicory extract in coffee extracts. According to these observers the extractives of roasted coffee contain 1.92 to 2.64% of reducing sugars, while the extractives of roasted chicory contain 25.2 to 27.7%. The test is not affected by the presence of cane sugar which is detected polarimetrically. More than 3% reducing sugars calculated on the extractives indicates the presence of chicory extract (see also Tatlock and Thomson, *J. Soc. Chem., Ind.*, 1910, 23, 138).

**Coffee Extracts.**—With regard to the examination of coffee essences and extracts for preservatives, Lythgoe and Marsh<sup>2</sup> point out that the ethereal extract of pure coffee essence gives a buff-coloured precipitate with ferric chloride solution and this may be mistaken for the precipitate given by benzoic acid. The ammonium salt of this substance, however, differs from ammonium benzoate in forming insoluble compounds with salts of manganese, nickel, magnesium, calcium, barium, and strontium. The following test for benzoic acid is based on this difference. Extract the acidified coffee solution with ether and shake the ethereal layer with dilute ammonia solution. Evaporate the ammoniacal solution to small bulk, add manganese sulphate solution, filter, and test the filtrate for benzoic acid with ferric chloride.

**Kola.**—Galenical preparations of kola are rather difficult to assay for caffeine owing to the formation of persistent emulsions when the preparations are shaken with chloroform and alkali. According to G. Meillière<sup>3</sup> the formation of such emulsions may be avoided by the use of the following method. 2.5 grm. of kola extract or 25 grm. of the fluid extract evaporated to small bulk are dissolved in 25 c.c. of simple syrup, transferred to a 250 c.c. separating funnel and treated with 2.5 grm. of potassium hydrogen carbonate. The froth produced by the brisk effervescence is easily broken down by adding chloroform of which 10 to 20 times the volume of the syrup is used in successive portions for the extraction. The chloroform solution is filtered and evaporated for alkaloids.

François,<sup>4</sup> on the other hand, recommends triturating with magnesia,

<sup>1</sup> *Amer. J. Pharm.*, 1913, 85, 535.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1911, 3, 842.

<sup>3</sup> *J. Pharm. Chem.*, 1912, 5, 438.

<sup>4</sup> *J. Pharm. Chim.*, 1913, 8, 411.

drying over sulphuric acid, and extracting with chloroform. It is doubtful (see Vol. VI, p. 591) whether the extraction would be complete by this method.

#### ERRATA IN VOL. VI.

Pages 580 and 581. The last line but one of page 581 should be transferred to page 580, so as to read as the second line from the bottom on this page.

Page 592, line 16 from bottom, 896 should read 1896.

Page 595, line 14, 38.5% should read 38.1%.

Page 647. Coffearine is said by Gorter (*Annalen*, 1910, 372, 239) to be identical with trigonellin.

Page 662. Mr. A. E. Johnson informs the editors that the method of estimating the percentage of coffee in coffee mixtures attributed to him is really due to E. W. Jones, who used it in obtaining the results recorded in the *Analyst*, 1882, 7, 76, in the case of the Birkenhead "Coffee" samples. The mistake has arisen in consequence of the method having been originally given in the First Edition of Johnson's "Analyst's Laboratory Companion."

# OTHER VEGETABLE ALKALOIDS.

By GEORGE BARGER, M. A., D. Sc. AND A. J. EWINS, D. Sc.

## Alkaloids of Colchicum.

The colloidal nature of aqueous solutions of colchicine has been shown by Zeisel and Stockert<sup>1</sup> to be only apparent. Determination of the molecular weight in acetic acid or in boiling ethylene dibromide gave normal values for the formula  $C_{22}H_{25}O_6N$ . In cold ethylene dibromide or in water somewhat higher values were obtained.

Zeisel and Stockert<sup>2</sup> have obtained the following new bromo-derivatives:

A *monobromide*,  $C_{22}H_{24}O_6NBr$ , MeOH, crystallised from methyl alcohol, m. p.  $151-155^\circ$  ( $133-135^\circ$  in sealed capillary). It is obtained by treating a dilute aqueous solution of colchicine with one molecular proportion of hydrobromic acid.

A *dibromo-derivative*,  $C_{22}H_{23}O_6NBr_2$ , m. p.  $146-150^\circ$  ( $125^\circ$ , sealed capillary) produced in the presence of an excess of hydrobromic acid.

A *tribromo-colchicine*,  $C_{22}H_{22}O_6NBr_3$ , m. p.  $131^\circ$  ( $118-122^\circ$  in sealed capillary) is obtained when a methyl alcoholic solution of colchicine is treated with excess of bromine.

*Tribromo-colchiceine*,  $C_{21}H_{20}O_6NBr_3 \cdot H_2O$ , and tribromotrimethyl-colchicinic acid,  $C_{19}H_{18}O_5NBr_3$ , were also obtained.

The physiological action of some derivatives of colchicine has been investigated by Fühner.<sup>3</sup>

In descending order of activity they may be arranged as follows: 1. colchicine (trimethylacetylcolchicinic acid); 2. trimethylcolchicinic acid methyl ether; 3. trimethylcolchicinic acid; 4. colchiceine (dimethylacetylcolchicinic acid). Replacement of the acetyl group of colchicine by benzoyl gives rise to a product the activity of which is about one-tenth that of colchicine. Oxycolchicine,  $C_{22}H_{23}O_7N$ , m. p.  $266-268^\circ$  obtained by the action of chromic acid on colchicine has an action on frogs, similar to that of veratrine, but has no action on mammals.

## Alkaloid of Laburnum and Furze.

**Cytisine.**—The constitution of cytisine has been recently further investigated by Ewins.<sup>5</sup> It had previously been found by Freund and his collaborators<sup>6</sup> that on treatment with hydriodic acid and phosphorus at

<sup>1</sup> *Monatsh.*, 1913, 34, 1327.

<sup>2</sup> *Monatsh.*, 1913, 34, 1339.

<sup>3</sup> *Arch. exp. Path. Pharm.*, 1913, 72, 228.

<sup>4</sup> *Monatsh.*, 1913, 34, 1181.

<sup>5</sup> *Trans.*, 1913, 103, 97.

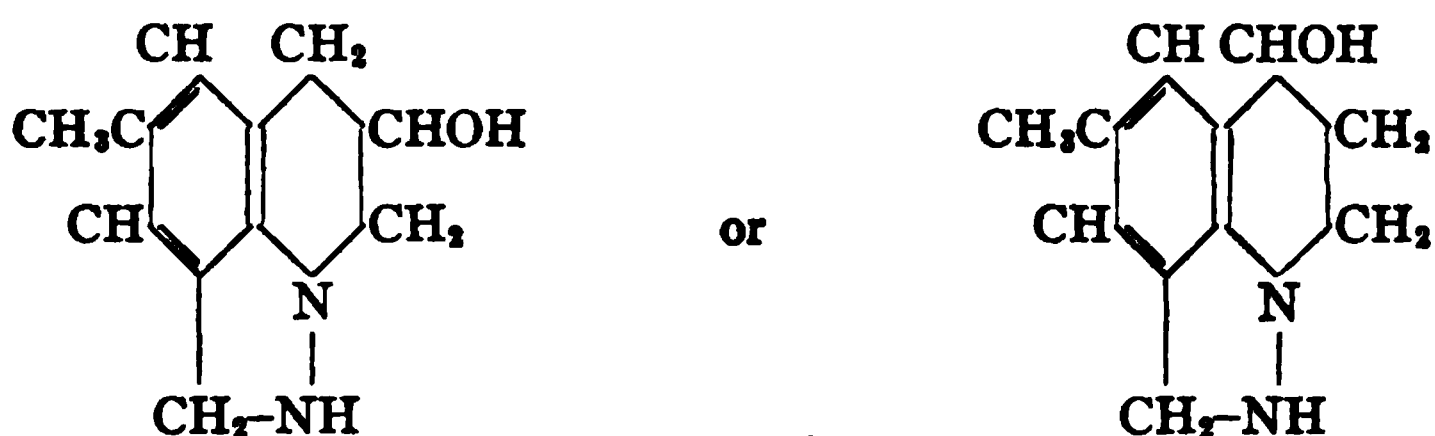
<sup>6</sup> *Ber.*, 1901, 34, 615; 1904, 37, 16; 1906, 39, 814.



about  $230^{\circ}$ , cytisine yielded among other products (a) a feebly basic crystalline solid *cytisoline*,  $C_{11}H_{11}ON$ , m. p.  $198^{\circ}$ , which, on reduction with sodium and alcohol gave a basic oil,  $\alpha$ -cytisolidine  $C_{11}H_{15}N$  and (b) a basic oil,  $\beta$ -cytisolidine, which was considered by Freund to be isomeric with  $\alpha$ -cytisolidine.

It has now been shown, however, (Ewins, *loc. cit.*) that  $\beta$ -cytisolidine has the composition  $C_{11}H_{11}N$  and this base was identified, by comparison with the synthetic product, as 6:8-dimethylquinoline. Further  $\alpha$ -cytisolidine,  $C_{11}H_{15}N$ , was shown to be the corresponding tetra-hydro. derivative, namely, 6:8-dimethyltetrahydroquinoline. Cytisoline,  $C_{11}H_{11}ON$ , from which  $\alpha$ -cytisolidine is produced on reduction, must, therefore, be a hydroxy-6:8-dimethylquinoline. It is not phenolic in character, nor is it identical with 2-hydroxy-6:8-dimethylquinoline and must, therefore, be either 3, or 4-hydroxy-6:8-dimethylquinoline.

Cytisoline,  $C_{11}H_{11}ON$ , differs in composition from cytisine,  $C_{11}H_{14}ON_2$ , only by the elements of ammonia. On this account it is suggested that cytisine may be formed by the fusion of three rings (benzene-pyridine-pyrazole) somewhat as shown



A compound so constituted might conceivably lose ammonia to form dimethylquinoline derivatives, but there is no direct evidence that cytisine has this constitution.

*N*-Methylcytisine,  $C_{12}H_{16}ON_2$ , hitherto only obtained by methylation of cytisine has recently been found<sup>1</sup> to occur naturally in the rhizome and roots of *Caulophyllum Thalictroides* (Linné) Michaux (Nat. Ord. Berberidaceæ) a plant indigenous to North America. For the isolation of the alkaloid the powdered material was first completely extracted with alcohol, the bulk of the solvent removed by distillation and the dark coloured viscid residue distilled with steam. The aqueous distillation residue was then purified by shaking thoroughly with amyl alcohol and with ether and finally precipitated with a slight excess of basic lead acetate. After removal of the excess of lead the liquid was made alkaline with sodium hydroxide and repeatedly extracted with chloroform. The residue after removal of the chloroform was converted into the hydrochloride, which was obtained crystalline from a mixture of ethyl acetate and alcohol. From the pure hydrochloride the base was obtained by dissolving in water and extracting with chloroform after making alkaline with sodium hydroxide. On evaporation of the chloroform, the

<sup>1</sup> Power and Salway, *Trans.*, 1913, 103, 194.

base solidified and was recrystallised from benzene and light petroleum. The yield from 22 kilos of material was about 5 grm. (0.23%).

*Methylcytisine* forms colourless prismatic needles m. p.  $137^{\circ}$ . It is readily soluble in water, alcohol, chloroform, and benzene, and is optically active,  $[\alpha]_D = -221.6^{\circ}$  in aqueous solution. The *hydrochloride*, B,  $(\text{HCl})_1, \text{H}_2\text{O}$  forms colourless prisms, m. p.  $250 - 255^{\circ}$  (decomp.). The *aurichloride*, B,  $\text{HAuCl}_4$ , crystallises in golden yellow needles m. p.  $205^{\circ}$  (decomp.) and the *picrate* forms long yellow needles m. p.  $228^{\circ}$  (after sintering from  $220^{\circ}$ ).

For the *assay* of the alkaloid in the drug the following procedure was found to give reliable and consistent results.

20 grm. of caulophyllum in No. 60 powder were treated with 100 c.c. of chloroform and 10 c.c. of a 10% aqueous sodium carbonate solution, and the mixture was vigorously shaken from time to time during 4 hours. The mixture was filtered and 50 c.c. of the filtrate transferred to a separating funnel and shaken with 10 c.c. of *N*/10 sulphuric acid. The acid liquid was separated and the chloroform again shaken with 10 c.c. of *N*/10 sulphuric acid. The acid solutions were mixed, extracted with 20 c.c. of ether and, after separating the ether, 5 c.c. of 10% sodium carbonate solution were added. The alkaline liquid was extracted three times with successive quantities of 20 c.c. of chloroform; the extracts were combined, washed twice with water (2 c.c. each time) and the chloroform was distilled off. The residual alkaloid was dissolved in 10 c.c. of *N*/50 sulphuric acid, 10 c.c. of ether were added and the excess of sulphuric acid was determined by titration with *N*/50 barium hydroxide (iodoeosin indicator). Two estimations gave 0.086% and 0.078% respectively.

According to Laidlaw (quoted by Power and Salway, *loc. cit.*) methylcytisine is very similar in its action to cytisine,<sup>1</sup> but is very much less active, the effect on the blood-pressure of the cat being about one-tenth as powerful as that of cytisine.

### The Alkaloids of Calabar.

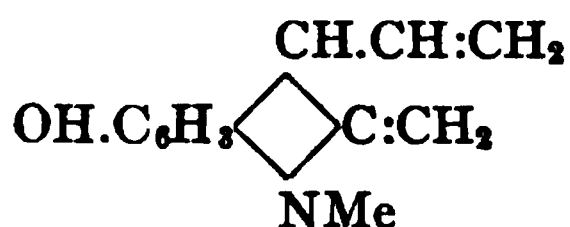
**Physostigmine (Eserine).**—Further work on the constitution of this alkaloid<sup>2</sup> has shown that eserine,  $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}_3$ , when heated *in vacuo* at  $150^{\circ}$  decomposes, giving eseroline,  $\text{C}_{13}\text{H}_{18}\text{ON}_2$ , which can then be distilled without undergoing any decomposition at a temperature of  $240^{\circ}$ . Eseroline yields a very characteristic benzoate, B,  $\text{C}_6\text{H}_5\text{COOH}$ , which crystallises in leaflets, m. p.  $155-156^{\circ}$ , and is obtained by adding solid benzoic acid to an ethereal solution of the base. Eseroline *picrate*, B,  $\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ , appears to be dimorphous, usually melting at  $167-168^{\circ}$ , but occasionally at  $190-191^{\circ}$ .

By the distillation of methyl eserolinium carbonate in a good vacuum (oil pump) a distillate is obtained which can be separated into two products:

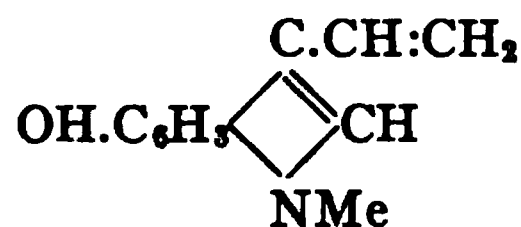
(1) a basic compound which is believed to have the constitution denoted by the formula

<sup>1</sup> Dale and Laidlaw, *J. Pharmacol. Exp. Therap.*, 1912, 3, 205.

<sup>2</sup> Straus, *Annalen*, 1913, 401, 350.



and (2) a phenolic base *physostigmol* to which the formula



is assigned. It is optically inactive and gives a *picrate* crystallising in red needles m. p. 161–162°. Ethylamine and dimethylamine were also obtained.

Physostigmine forms an aurichloride, B, 2HAuCl<sub>4</sub>, yellow leaflets, m. p. 163–165° and a platinichloride, B, H<sub>2</sub>PtCl<sub>6</sub>, orange yellow needles, m. p. 180° (decomp.).

### Alkaloids of Ergot.

Recent unpublished observations have thrown much doubt on the statement on page 20, Vol. VII, that ergotoxine contains a carboxyl group. The figures 4 and 5 do not represent salts of ergotoxine ethyl ester, but of ergotoxine itself. Thus the phosphate at least appears to occur in two crystalline forms.

### The Alkaloids of Jaborandi.

The leaves of *Pilocarpus microphyllus* contain the alkaloids pilocarpine and isopilocarpine, but no pilocarpidine.<sup>1</sup> After removing the first two mentioned bases as completely as possible there still remains a residue which consists of a mixture of bases. From this mixture a new alkaloid *pilosine* (carpine) has recently been isolated by Pyman<sup>2</sup> and almost simultaneously by Léger and Roques.<sup>3</sup>

The isolation of pilosine was carried out by Pyman in the following manner. The residual syrup (after complete extraction of pilocarpine and isopilocarpine) from several tons of leaves was diluted with water, and the bases precipitated by addition of ammonia. There was first precipitated a dark coloured oil and later a lighter coloured oil. These fractions were redissolved in dilute acid, and again fractionally precipitated by ammonia when the impurities became concentrated in the earlier dark coloured fractions. The latter fractions of the sparingly soluble oily precipitate when dissolved in a little alcohol readily deposited crystals of the new base pilosine. Purification was effected by recrystallisation from alcohol.

Léger and Roques proceed as follows: Pilocarpine and isopilocarpine were removed as completely as possible as nitrates or hydrochlorides. The residual bases were precipitated by ammonia and the first fractions of the

<sup>1</sup> Jowett, *Trans.*, 1900, 77, 473.

<sup>2</sup> *Trans.*, 1912, 101, 2260.

<sup>3</sup> *Compt. Rend.*, 1912, 155, 1088.

precipitate purified first by crystallisation from absolute alcohol and later from 90% alcohol.

According to Pyman the amount of pilosine present in the leaves of *Pilocarpus microphyllus* amounts to about 0.007%. No other alkaloid is present in amount greater than 0.003%. The absence of pilocarpidine was also confirmed.

*Pilosine*,  $C_{16}H_{18}O_3N_2$ , crystallises from alcohol in colourless plates, m. p.  $187^\circ$  (corr.) (Pyman); in prisms, m. p.  $184^\circ$ – $185^\circ$  (Léger Roques). It is sparingly soluble in cold water, chloroform, ether, ethyl acetate and benzene, but fairly readily soluble in hot water or alcohol. The base is dextrorotatory. In chloroform it has  $[\alpha]_D + 40.2^\circ$ , in alcohol  $[\alpha]_D + 39.9^\circ$ . It is a feeble monacid base and does not readily form crystalline salts, although several have been prepared and described. Like pilocarpine it contains a lactone group and hence dissolves in hot caustic alkalis. It gives no colouration with sodium diazobenzene-*p*-sulphonate.

*Pilosine sulphate*,  $(B)_2 \cdot H_2SO_4$ , crystallises from alcohol in plates, m. p.  $194^\circ$ – $195^\circ$  (corr.). The *hydrogen tartrate*  $B \cdot C_4H_6O_6$ , separates from alcohol as an oil which slowly crystallises and melts at  $135^\circ$ – $136^\circ$  (corr.). The *aurichloride*,  $B \cdot HAuCl_4$ , crystallises from glacial acetic acid in golden-yellow wedge-shaped plates, m. p.  $143^\circ$ – $144^\circ$ . A crystalline *hydrochloride*,  $B \cdot HCl$ , a *platinichloride*,  $B \cdot H_2PtCl_6 \cdot 5H_2O$ , and a *methiodide*,  $B \cdot CH_3I$ , crystallising in pale yellow prisms have also been described.

On treatment with acetic anhydride (best by boiling with a mixture of equal parts of acetic anhydride and glacial acetic acid) pilosine loses the elements of water and a new base, *anhydro-pilosine*, which yields well crystalline salts, is produced.

*Anhydro-pilosine*,  $C_{16}H_{16}O_2N_2$ , crystallises from ethyl acetate in colourless rods, m. p.  $133^\circ$ – $134^\circ$  (corr.). It is sparingly soluble in cold, easily soluble in hot water, and in the usual organic solvents with the exception of ether. The base is unsaturated, contains a lactone group, and is optically active. In alcoholic solution it has  $[\alpha]_D + 66.2^\circ$ .

The *sulphate*,  $B_2 \cdot H_2SO_4$ , prisms m. p.  $174^\circ$  (corr.), the *nitrate*,  $B \cdot HNO_3$ , prisms m. p.  $153^\circ$ – $154^\circ$  (corr.) and *hydrogen oxalate*,  $B \cdot C_2H_2O_4$ , needles m. p.  $153^\circ$ – $154^\circ$  (corr.) have been described. *Pilosinine*,  $C_9H_{12}O_2N_2$ , is obtained when pilosine is distilled with 20% aqueous potassium hydroxide solution, benzaldehyde being produced at the same time. In order to isolate the base the alkaline distillation residue is rendered acid and boiled for a few minutes, to reform the lactone group. The solution is then made alkaline with ammonia, and the base is extracted with chloroform and converted into the crystalline nitrate. From a solution of the nitrate the pure base is obtained by extraction with chloroform after addition of ammonia.

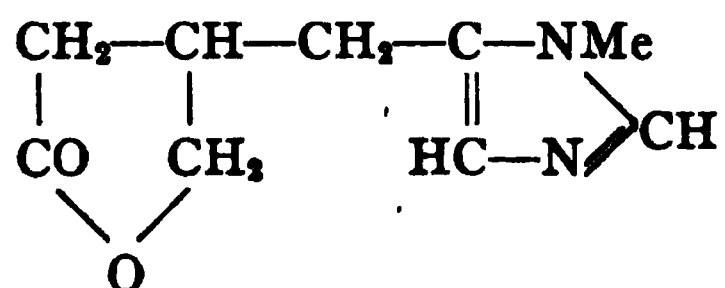
*Pilosinine* crystallises from ethyl acetate in plates, m. p.  $78^\circ$ – $79^\circ$  (corr.). It is somewhat deliquescent, readily soluble in water, alcohol, chloroform, and hot ethyl acetate, sparingly soluble in dry ether. The base may be

distilled at about  $300^{\circ}$  (35 mm.). It is optically active; in freshly prepared aqueous solution it has  $[\alpha]_D + 41.2^{\circ}$ . As in the case of pilocarpine, however, the rotation rapidly falls on keeping, presumably owing to the conversion of the lactone into a hydroxy-acid.

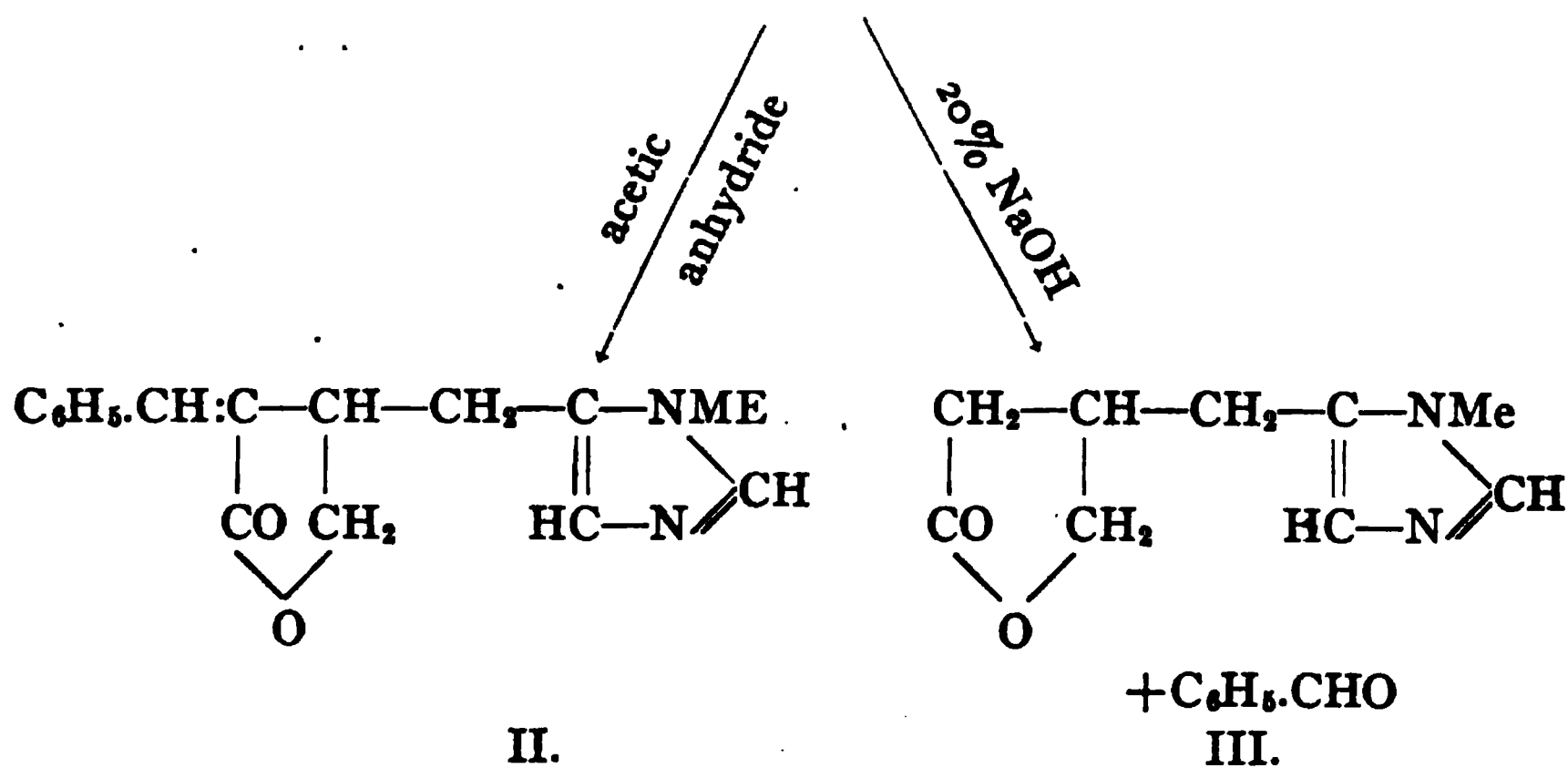
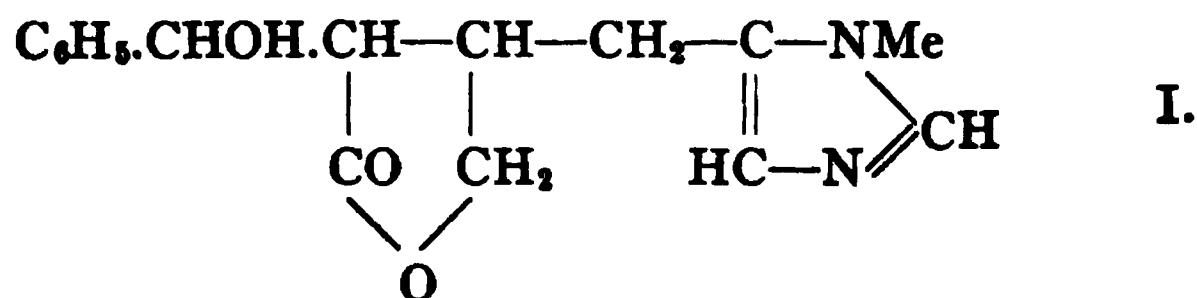
The *nitrate*,  $B, HNO_3$ , prisms m. p.  $165^{\circ}$ – $167^{\circ}$  (corr.) and the *hydrochloride*,  $B, HCl$ , prismatic needles m. p.  $218^{\circ}$ – $219^{\circ}$  (corr.) are readily obtained.

Both anhydro-pilosine and pilosinine are also obtained by heating pilosine with water to  $140^{\circ}$  for 10 hours.<sup>1</sup>

**Constitution of Pilosine.**—The chemical and physiological properties of pilosinine very closely resemble those of pilocarpine. Moreover pilosine, the parent base of pilosinine, occurs in the same plant as pilocarpine and isopilocarpine, and it therefore appears highly probable that pilosinine is a glyoxaline derivative closely analogous to pilocarpine. Bearing these facts in mind, the constitution of pilosinine may be satisfactorily represented by the formula



Further, from the facts that on distillation with strong aqueous sodium hydroxide pilosine yields benzaldehyde and pilosinine, and that by removal of the elements of water from pilosine the unsaturated base anhydropilosine is produced, Pyman concludes that pilosine must have the constitution denoted by the formula (I)



<sup>1</sup> Léger and Roques, *Compt. rend.*, 1913, 156, 1687.

The formation of anhydro-pilosine (II) and of pilosinine (III) is satisfactorily represented as shown. The decomposition of pilosine into benzaldehyde and pilosinine by alkali is supported by the fact that pilosine is, on the above assumption, the lactone of a  $\beta$ -hydroxy-acid which under certain circumstances is known to be decomposed by alkali forming an aldehyde and an acid.

**Physiological Action.**—According to Laidlaw (quoted by Pyman), pilosine and anhydro-pilosine have a very feeble pilocarpine-like action, in that they produce (in 20 mg. doses) a weak inhibition of the cat's heart. Pilosinine, however, has a more marked, though mild, pilocarpine action inhibiting the heart of cats and frogs and producing some salivary secretion.

### Solanine Alkaloids.

A recent investigation of the constituents of *Solanum angustifolium* by Tutin and Clewer<sup>1</sup> has resulted in the isolation of a new solanine base, a gluco-alkaloid to which the authors have given the name solangustine. *Solanum angustifolium* occurs in several countries in South America, where it is known as "Duraznillo Blanco" and is employed as a febrifuge, chiefly in the treatment of enteric fever. The material employed was obtained from Lima (Peru) and was botanically identified.

For the isolation of the alkaloid the following procedure was adopted: The completely dried material (leaves, twigs, and flowers) was completely extracted with hot alcohol. The residue after removal of the solvent was mixed with water and distilled with steam to remove the last traces of alcohol. The residual aqueous liquid was removed from the resin and the liquid extracted with amyl alcohol. The numerous extracts were combined, washed with water, and concentrated. The residue was then distilled with steam to remove amyl alcohol completely, and the dark-coloured aqueous liquid extracted several times with ether to remove impurities. The solution was then treated with about 5% of its weight of sulphuric acid, warmed gently for 15 minutes, cooled and the precipitated sulphate filtered off. For further purification it was well washed with boiling alcohol, and then digested with slightly diluted acetic acid when, without dissolving to any appreciable extent, it became crystalline. From the sulphate the free base was obtained by treating with warm sodium carbonate solution and extracting with warm amyl alcohol. The washed amyl alcohol solution on concentration deposited the free base as hard pale yellow aggregates of crystals. The amount present was about 0.065% of the dried material.

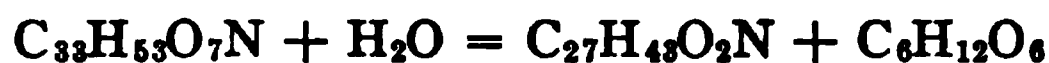
**Solangustine**,  $C_{33}H_{53}O_7N \cdot H_2O$ , darkens at 225° and melts at 235° (decomp.). It contains 1  $H_2O$  and when anhydrous rapidly reabsorbs water from the air. The base is characterised by extreme insolubility in nearly all solvents and by the insolubility of its salts. Solangustine dissolves fairly readily in pyridine, but scarcely at all in any other solvent.

<sup>1</sup> *Trans.*, 1914, 105, 564.



It contains no methoxyl group, and does not yield a crystalline acetyl derivative. The only crystalline salt obtained was the sulphate  $B_2, H_2SO_4, 3H_2O$ . On shaking an amyl alcohol solution of the base with dilute sulphuric acid it separates as small acicular crystals which do not melt or decompose up to  $325^\circ$ . It crystallises with  $3H_2O$  and when anhydrous is very hygroscopic.

On hydrolysis solangustine yields dextrose and an amorphous base *solangustidine*,  $C_{27}H_{43}O_2N$ , which forms crystalline salts. The hydrolysis is thus represented:



*Solangustidine*,  $C_{27}H_{43}O_2N$ , is insoluble in water, soluble in dilute alcohol, from which it separates in amorphous granules. On treatment with acetic anhydride, *acetylsolangustidine*,  $C_{27}H_{42}O_2N \cdot Ac$ , crystallising from ethyl acetate in needles, m. p.  $256^\circ$ , is obtained. This compound is remarkable for its stability towards alkalis, being recovered unchanged after several hours' heating with alcoholic potassium hydroxide.

Solangustidine forms well crystalline salts which are practically insoluble in water.

The *hydrochloride*,  $B, HCl$ , crystallises from alcohol (containing a little alcoholic  $HCl$ ) in lustrous plates, m. p. above  $325^\circ$ . It is sparingly soluble in amyl alcohol or hot ethyl alcohol.

The *hydrobromide*,  $B, HBr$  forms plates, m. p.  $320^\circ$  (decomp.). It is rather more readily soluble in alcohol than the hydrochloride.

The *nitrate*,  $B, HNO_3$ , is fairly soluble in hot dilute nitric acid. It darkens at  $260^\circ$  and decomposes at  $290^\circ$ .

The *sulphate*,  $B_2, H_2SO_4$ , was obtained crystalline by boiling the amorphous precipitate, obtained by treating an alcoholic solution of solangustidine with dilute sulphuric acid, for some time. Colourless leaflets, m. p. above  $330^\circ$ . Sparingly soluble in water.

The *picrate*,  $B, C_6H_3O_7N_3$ , forms yellow needles, m. p.  $250^\circ$  (decomp.).

### The Alkaloid of the Common Broom.

**Sparteine**,  $C_{15}H_{26}N_2$ .—A number of salts of this base have been described by Corriez.<sup>1</sup> Among them *sparteine perbromide*,  $C_{15}H_{26}H_2, 2HBr, Br_2, H_2O$ , is obtained by the action of bromine on sparteine, in fuming hydrobromic acid solution. The salt forms small yellow crystals, m. p.  $193^\circ$ , and its formation constitutes a delicate *test* for sparteine, since it is stated to be produced in a dilution of one part in ten thousand.

### Alkaloids of Ipecacuanha.

The interest attached to these alkaloids has recently been greatly increased by the discovery by Vedder<sup>2</sup> of the intensely toxic action of emetine

<sup>1</sup> *Bull. Sc. Pharmacol.*, 1912, 19, 468–480 and 533–540.

<sup>2</sup> *Journ. Trop. Med.*, 1911, 14, 149 (abstr.).



on amoebæ, and its therapeutic application by Rogers<sup>1</sup> to the treatment of amoebic dysentery (hypodermic injection of the hydrochloride). As a result several papers dealing mainly with the constitution and characterisation of these alkaloids have appeared during the last 2 years.

Of these, perhaps the most important publication is that of Carr and Pyman.<sup>2</sup> These authors have fully investigated the subject of the ipecacuanha alkaloids with the result that much of the older work must now be discredited. In particular they have succeeded in establishing the relationship existing between the three alkaloids emetine, cephaeline, and psychotrine and have thrown some light on their constitution.

From the results of a very large number of analyses of the pure bases and of their respective salts they reject the older formulæ assigned by various workers to these alkaloids and adopt the following: emetine,  $C_{29}H_{40}O_4N_2$ ; cephaeline,  $C_{28}H_{38}O_4N_2$ ; psychotrine,  $C_{28}H_{36}O_4N_2$ . Emetine is, therefore, cephaeline +  $CH_2$ , and cephaeline is psychotrine +  $H_2$ . This relationship was indeed confirmed experimentally, since psychotrine on reduction gave two isomeric dihydro derivatives one of which was identical with cephaeline, while cephaeline in turn on methylation under suitable conditions gave, among other products, a base which was identified as emetine.

The material used in their investigation was Brazilian ipecacuanha root which contained 2.7% of total alkaloids. From this they obtained 1.35% of pure emetine, 0.25% of cephaeline, and a small amount of psychotrine. The method employed to isolate the alkaloids was that originally described by Paul and Cownley.<sup>3</sup>

A recent paper by Hesse<sup>4</sup> describes two new alkaloids, *ipecamine*,  $C_{28}H_{36}O_4N_2$ , and *hydro-ipecamine*,  $C_{28}H_{38}O_4N_2$ , in addition to those already mentioned, but these are amorphous and are at present not sufficiently well characterised to warrant unhesitating acceptance. To emetine he assigns the old formula  $C_{30}H_{40}O_5N_2$  originally proposed by Kunz Krause, which was arrived at from analyses of what was undoubtedly a mixture of emetine and cephaeline.

The following description of the alkaloids emetine, cephaeline, and psychotrine is based on Carr and Pyman's paper.

**Emetine**,  $C_{29}H_{40}O_4N_2$ , m. p.  $74^\circ$  (corr.), has not so far been crystallised. It is obtained as a white amorphous powder by treatment of solutions of its salts with dilute alkalis, or as a varnish by the spontaneous evaporation of its solutions in organic solvents. It is readily soluble in methyl, ethyl, or amyl alcohol, in ethyl acetate, ether, acetone, or chloroform; less soluble in benzene or light petroleum. Molecular weight determinations and titration experiments support the view that the base contains two

<sup>1</sup> *Brit. Med. Journ.*, 1912, i, 1424.

<sup>2</sup> *Trans.*, 1914, 105, 1591.

<sup>3</sup> Vol. VII, p. 38.

<sup>4</sup> *Annalen*, 1914, 405, 1.

nitrogen atoms in the molecule, evidence of formation of basic salts having been obtained.

Emetine is lævorotatory. In chloroform solution it has  $[\alpha]_D - 49.7^\circ$ , and this is independent of the concentration. In dissociating solvents, however, its rotation varies considerably. The following salts were characterised:

The *hydrochloride*,  $B_2HCl \cdot 7H_2O$ , woolly needles from water. Crystallised from methyl alcohol the salt contains only  $3\frac{1}{2} H_2O$ . The anhydrous salt sinters at  $235^\circ$  and decomposes at  $255^\circ$  (corr.). A saturated aqueous solution at  $18^\circ$  contains 13.1 gm. of hydrated salt in 100 c.c. of solution.

The *hydrobromide*,  $B_2HBr \cdot 4H_2O$ , long slender needles from water. Sinters at  $245^\circ$  and melts from  $250^\circ$ – $265^\circ$  (corr.). Sparingly soluble in cold, readily soluble in hot water. 100 c.c. of a saturated solution at  $18^\circ$  contains 1.9 gm. of hydrated salt.

The *hydriodide*,  $B_2HI \cdot 3H_2O$ , crystallises from alcohol in needles and is sparingly soluble in water. It sinters from  $230^\circ$  and melts at  $235^\circ$ – $238^\circ$  (corr.).

The *nitrate*,  $B_2HNO_3 \cdot 3H_2O$ , crystallises from water or alcohol in fine needles. It sinters from  $188^\circ$  and gradually melts up to  $245^\circ$  (corr.). It is sparingly soluble in water.

The *sulphate*,  $B_2H_2SO_4 \cdot 7H_2O$ , forms white woolly needles and is very soluble in water. It sinters at  $205^\circ$  and finally melts at  $245^\circ$  (corr.). The *acetate* and *platinichloride* were not obtained crystalline.

*Benzoylemetine*,  $C_{29}H_{39}O_4N_2OC \cdot C_6H_5$ , crystallises from alcohol in needles, m. p.  $185^\circ$ – $186^\circ$  (corr.). Keller's "benzoylemetine" appears to have been the benzoate of benzoylemetine.

**Cephaeline**,  $C_{28}H_{38}O_4N_2$ .—The pure base is best obtained by regenerating it from a pure salt (hydrochloride or hydrobromide) and subsequently recrystallising from ether. It forms colourless needles which, dried in the air, sinter at  $106^\circ$  and melt at  $115^\circ$ – $116^\circ$  (corr.). After drying at  $100^\circ$  it melts gradually from  $120^\circ$ – $130^\circ$ . It is readily soluble in chloroform, alcohol or acetone, sparingly so in ether or light petroleum. The base is apparently somewhat unstable. Its solutions darken on keeping and the base itself becomes coloured on drying at  $100^\circ$ . Cephaeline is lævorotatory. In chloroform solution it has  $[\alpha]_D - 43.4^\circ$ . The hydrochloride and hydrobromide were alone obtained crystalline.

The *hydrochloride*,  $B_2HCl \cdot 7H_2O$ , crystallises from dilute hydrochloric acid in stout prisms or from water as fine powdery crystals. The salt has no sharp melting point, but sinters at  $245^\circ$  and finally melts at  $270^\circ$  (corr.). A saturated aqueous solution at  $18^\circ$  contains 26.5 gm. of hydrated salt per 100 c.c.

An *acid hydrochloride*,  $B_5HCl$ , separates from strongly acid solutions in fine needles, m. p.  $84^\circ$ – $86^\circ$ .

The *hydrobromide*,  $B_2HBr \cdot 7H_2O$ , crystallises from dilute hydrobromic acid. It sinters at  $266^\circ$  and melts up to  $293^\circ$ . 100 c.c. of a saturated aqueous solution at  $18^\circ$  contains 5.4 gm. of anhydrous salt.

**Psychotrine**,  $C_{28}H_{36}O_4N_2$ , was first obtained by Paul and Cownley as yellow prisms, m. p.  $138^\circ$ . It crystallises from wet acetone or alcohol in large yellow prisms (with a blue fluorescence) which contain  $4H_2O$ . After drying at  $100^\circ$  it sinters at  $120^\circ$ , becomes transparent at  $124^\circ$ – $126^\circ$  (corr.) and melts at  $138^\circ$ . It is sparingly soluble in water, benzene, petroleum, or ether, more readily soluble in acetone, alcohol or chloroform. Its solutions in alkalis or strong acids are colourless. In concentrated sulphuric acid on addition of a trace of nitric acid it gives a sherry colour. With excess of Fröhde's reagent it yields a pale green solution.

The *sulphate*,  $B, H_2SO_4, 3H_2O$ , crystallises from water in faintly yellow scales. The anhydrous salt sinters at  $207^\circ$  and melts at  $214^\circ$ – $217^\circ$  (corr.).

The *nitrate*,  $B, 2HNO_3, H_2O$ , crystallises from water in silky needles, sparingly soluble in cold water. The anhydrous salt sinters from  $165^\circ$  and melts at  $184^\circ$ – $187^\circ$  (corr.).

The *hydriodide*,  $B, 2HI$ , crystallises from a slight excess of dilute hydriodic acid as sulphur-coloured microscopic needles which sinter from  $200^\circ$  and melt and decompose at  $220^\circ$  (corr.).

**Constitution of Ipecacuanha Alkaloids:**—As already mentioned, the relationship existing between emetine, cephaeline and psychotrine has been established by Carr and Pyman. Of the ultimate constitution of these bases little is known. It has been found, however,<sup>1</sup> that on oxidation with potassium permanganate emetine gives rise to 6:7-dimethylisoquinoline-1-carboxylic acid, and also to *m*-hemipinic acid and its imide. The alkaloids thus belong to the class of isoquinoline bases. Oxidation of emetine and of cephaeline with ferric chloride also gave rise to new bases which are of considerable interest from the point of view of the constitution of these alkaloids.

<sup>1</sup> Carr and Pyman, *Proc. Chem. Soc.*, 1913, 29, 226. See also Windaus and Hermanns, *Ber.*, 1914, 47, 1470.

# GLUCOSIDES.

By E. FRANKLAND ARMSTRONG.

**Synthetic Glucosides.**—A number of glucosides of the chalkones, of which two—naringenin and hesperitin—occur naturally in plants, have been synthesised by Bargellini.<sup>1</sup> Helicin was condensed with hydroxy-derivatives of acetophenone in alcoholic solution in presence of 40% sodium hydroxide or by heating in presence of piperidine.

Synthetic glucosides of the purine bases are described by Fischer and Helferich<sup>2</sup> including those of theophylline, theobromine, adenine and hypoxanthine. By combining these with phosphoric acid, products resembling the nucleotides have been obtained.

**Cyanogenetic Glucosides** (Compare Vol. VII, p. 101).—The cyanogenetic plants of New South Wales have been investigated by Petrie<sup>3</sup> using sodium picrate paper as an indicator of the presence of hydrogen cyanide. Of 60 species stated to contain such glucosides 20 are grasses.

**Phytosterolins.**—A number of glucosides of phytosterols have been isolated from plants of which sitosterol,  $C_{27}H_{48}O_6$ , and stigmasterol,  $C_{28}H_{48}O_6$ , are types. They have been investigated by Power and Salway<sup>4</sup> who give a list of the known varieties. They are not affected by heating with aqueous or dilute alcoholic hydrogen chloride, but are hydrolysed by this acid when dissolved in warm amyl alcohol solution. They form crystalline tetra-acetyl- and tetrabenzoyl-derivatives and give the characteristic colour indication of the phytosterols when they are dissolved in acetic anhydride and chloroform and a drop of concentrated sulphuric acid is added. Sitosterol-*d*-glucoside melts at 270–300°; it can be prepared synthetically from sitosterol and acetobromoglucose.<sup>5</sup> Glucosides of cholesterol and of fatty alcohols have been synthesised in the same manner; it is probable that they will be found in plants.

Seeing that the tannins are acyl-derivatives of glucose of the type of penta-acetyl glucose it was to be expected that simpler acyl derivatives would be found to exist naturally. The first of these to be described is a crystalline bitter substance present in the leaves and stems of *Daviesia latifolia*.<sup>6</sup> This is a dibenzoyl derivative ( $C_{25}H_{28}O_{12}$ ) of a disaccharide composed

<sup>1</sup> *Gazzetta*, 1914, 44, ii, 520.

<sup>2</sup> *Ber.*, 1914, 47, 210.

<sup>3</sup> *Chem. News*, 1914, 110, 126.

<sup>4</sup> *Trans.*, 1913, 103, 399.

<sup>5</sup> Salway, *Trans.*, 1913, 103, 1022–1029.

<sup>6</sup> Power and Salway, *Trans.*, 1914, 105, 767–778; 1062–1069.

of glucose and xylose, m. p. 147–148°. The glucoxylose has no reducing action on Fehling's solution and therefore is of the same type as saccharose.

Several species of the genus *Solanum* are reported to contain bases which are both alkaloids and glucosides. *Solangelustine*, the gluco-alkaloid isolated from *Solanum angustifolium* by Tutin and Clewer<sup>1</sup> has the composition  $C_{33}H_{53}O_7N$ , m. p. 235° (decomp.). It is hydrolysed to glucose and solangelustidine and is without physiological activity. The plant also contains quercetin, rutin and *l*-asparagine. Reference is given to similar gluco-alkaloids termed collectively solanines (see page 540).

**Digitalis** (Compare Vol. VII, p. 116).—According to Hirohashi<sup>2</sup> digitalis leaves gathered from different parts of the plant differ in their physiological effect, there being a diminution in the latter from the top downwards. The leaves are best collected before inflorescence. The flowers have a maximum of activity during budding; there is no difference in activity between red and white flowers. An infusion of the leaves can be evaporated without loss of any of its physiological effects.

Hatcher<sup>3</sup> states that digitalis of the first year's growth is probably as active as that of the second and the cultivated is as active as the wild-grown plant. When properly dried and stored, digitalis will keep indefinitely.

Martindale<sup>4</sup> claims that the following simple chemical method gives an approximate idea whether a tincture of digitalis is up to the physiological test requirements: 10 c.c. of the tincture are mixed with 10 c.c. of water and precipitated with 3 c.c. of 10% normal lead acetate solution, a little kieselguhr being added. After standing for 15 minutes the precipitate is filtered off and washed. The lead is removed from the filtrate by the addition of 2 c.c. of 10% sodium phosphate solution. The filtrate is evaporated to dryness after adding 0.2 grm. of calcium carbonate. The residue is mixed with sand and extracted five times with chloroform, using 10 c.c. on each occasion. The extract is evaporated and the residue extracted with warm water on the water-bath using 10 c.c. and 5 c.c. and again employing sand. The filtrate is evaporated to dryness and extracted three or four times with chloroform, 5 c.c. each time, the residue being mixed with sand and thoroughly triturated. The chloroform liquors are evaporated and the residue dissolved in 4 c.c. of glacial acetic acid. 0.1 c.c. of the acetic acid solution is mixed with 1 c.c. of "sulphuric ammonium molybdate solution" in a 5 × 1 cm. test-tube, and the depth of colour produced after 5 minutes is compared with a standard. The colouration indicates the content of combined "active water-soluble glucosides."

Reichard<sup>5</sup> describes a number of reactions of digitonin. A drop of cobalt nitrate solution is evaporated until a deep blue coloured residue is obtained; digitonin and a drop of glacial acetic acid are added and the mixture exposed

<sup>1</sup> *Trans.*, 1914, 105, 559.

<sup>2</sup> *Chem. and Drug.*, 1913, 82, 18.

<sup>3</sup> *Amer. J. Pharm.*, 1914, 86, 567.

<sup>4</sup> *Pharm. J.*, 1912, 35, 745, 778.

<sup>5</sup> *Pharm. Zentr.*, 1913, 54, 217.

to the air for 30 hours. A mass of red crystals is obtained whereas digitoxin only gives a green residue.

The digitonide of oxycholesterol, which occurs in animal fats in association with cholesterol, crystallises in rhombic plates, m. p.  $215^{\circ}$ .<sup>1</sup>

A new glucoside, Gitonin has been found in *Digitalinum germanicum*. It is separable from digitonin by taking advantage of its smaller solubility in 95% alcohol. It has the composition  $C_{26}H_{44}O_4$  or  $C_{26}H_{42}O_4$ , m. p.  $272^{\circ}$ ,  $[\alpha]_D - 50.7^{\circ}$  in pyridine. Acids hydrolyse it to galactose, a pentose and gitogenin, which has m. p.  $272^{\circ}$  and forms a *diacetate*, m. p.  $243-244^{\circ}$ .<sup>2</sup>

**Digitoxin and Gitalin.**<sup>3</sup>—When a solution of digitoxin, gitalin and anhydrogitalin in a mixture of equal volumes of chloroform and methyl alcohol is treated with ether, gitalin remains in solution and the two other constituents are precipitated.

**Strophanthin.**—According to Lampart and Müller<sup>4</sup> who have compared a number of methods, the most satisfactory way of determining Strophanthin in strophanthus seeds or tincture, is an extension of that of Cæsar and Loretz described in Vol. VII, p. 122. The full details are as follows:

“7.0 gm. of the finely crushed seeds are boiled in a reflux apparatus for an hour with 70.0 gm. of absolute alcohol. When cold, the whole is made up to the original weight with absolute alcohol, and 50.5 gm. filtered into a porcelain basin. The alcohol is evaporated and the residue washed with light petroleum which is poured through a filter. The insoluble residues in the filter and basin are boiled with 5–8 gm. of water, treated with 5 drops of lead acetate solution and about 0.2 gm. of kieselguhr, well mixed and filtered into a 100 c.c. flask. The insoluble portion is washed till the runnings no longer have a bitter taste. The filtrate is treated with 5 drops of hydrochloric acid and boiled gently for 2 hours, the volume being kept between 10–20 c.c. by the addition of distilled water. When cold, the liquid is extracted twice with 10 c.c. of chloroform, which is filtered into a tared flask. The aqueous portion is again boiled for half an hour, cooled and extracted three times with 10 c.c. of chloroform. If the aqueous portion after warming still tastes bitter, the boiling and extraction with chloroform are repeated. The chloroform is distilled off, the residue dried in a desiccator and then weighed. It consists of strophanthidin, 1 part of which corresponds to 2.187 parts of pure strophanthin. For the tincture 51 gm. (equivalent to 5.0 gm. of the seeds) are heated on the water-bath to remove the alcohol, the residue is taken up with 20 gm. of hot water, treated with 15 drops of lead acetate solution and 0.2 gm. of kieselguhr. It is then treated by the method described above for the seeds.”

The new method gives higher percentages than any of the others.

All varieties of the drug contain varying proportions up to 0.2% of the hæmolytic saponin, strophanthic acid.<sup>5</sup> This forms precipitates with salts

<sup>1</sup> Lifschutz and Grethe, *Ber.*, 1914, 47, 1453.

<sup>2</sup> Windaus and Schnechenburger, *Ber.*, 1913, 46, 2628.

<sup>3</sup> See Kraft, *Arch. Pharm.*, 1912, 250, 118, and Kiliani, *Ibid.*, 1913, 251, 562.

<sup>4</sup> *Arch. Pharm.*, 1913, 251, 609.

<sup>5</sup> Sieburg, *Ber. Pharm. Ges.*, 1913, 23, 278.

of heavy metals; it is hydrolysed to glucose and strophanthigenin. A list of colour reactions is given (see also Chem. Soc. Abstracts, 1913, i, 640) which distinguish strophanthic acid from strophanthin.

**Sarsaparilla.**—Sarsaparilla root has been fully investigated by Power and Salway<sup>1</sup> who worked with the grey Jamaica root of the British Pharmacopœia (*Smilax ornata*). The following compounds were obtained from the alcoholic extract:

- (1) *Sarsasaponin*, a crystalline glucoside— $C_{44}H_{76}O_{20}$  (m. p.  $248^{\circ}$ ,  $[\alpha]_D - 48.5^{\circ}$ ) yielding glucose and sarsasapogenin on hydrolysis.
- (2) *Sitosterol-d-glucoside* (a phytosterolin)— $C_{32}H_{56}O_8$  (m. p.  $280-285^{\circ}$ ).
- (3) *Sitosterol*,  $C_{27}H_{48}O$  (m. p.  $135-136^{\circ}$ ,  $[\alpha]_D - 27.3^{\circ}$ ).
- (4) *Stigmasterol*,  $C_{30}H_{50}O$  which is identified by its tetrabromoacetyl derivative,  $C_{30}H_{49}OBr_4.COCH_3$  (m. p.  $208^{\circ}$ ).
- (5) *Sarsapic Acid*—a new crystalline dicarboxylic acid (m. p.  $305^{\circ}$ ),  $C_4H_2O_2(CO_2H)_2$ .
- (6) *Glucose*.
- (7) *Fatty Acids*—viz., palmitic, stearic, behenic, oleic and linoleic acids.
- (8) *Cetyl-d-glucoside*.
- (9) Potassium nitrate.

The root contains a small quantity of an enzyme of the emulsin type.

Inasmuch as only one definite saponin glucoside is present, it is considered that the parillin of earlier investigators consisted of a mixture of sarsasaponin and a phytosterolin. Commercial smilacin represents a relatively small proportion of sarsasaponin with indefinite amorphous products.

<sup>1</sup> *Trans.*, 1914, 105, 201-209.



# NON-GLUCOSIDAL BITTER PRINCIPLES.

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By G. C. JONES, F. I. C.

## Aloes.

**Detection of Aloes in Extracts of Drugs Containing Hydroxy-methyl-anthraquinones** (cf. Vol. VII, pp. 149-150).—The following method will detect as little as 0.2 grm. of aloes extract in 5 grm. of a mixture of extracts of rhubarb, frangula and cascara sagrada.<sup>1</sup> The alcoholic extract is evaporated to expel the alcohol, the residue taken up in water and the liquid filtered. The filtrate (100 c.c.) is heated for 30 minutes on the water-bath with 5 c.c. of 10% sulphuric acid, the sulphuric acid precipitated with the exact amount of barium hydroxide solution, and the filtrate from the barium precipitate concentrated to 100 c.c. and clarified with lead acetate solution, care being taken to avoid a large excess. Of the solution, 10 c.c. is filtered, freed from lead by means of sodium sulphate solution or dilute sulphuric acid and divided into two portions. One of these is shaken with 5 c.c. of benzene and the benzene extract shaken with dilute ammonia. If the hydroxymethylanthraquinones have been completely precipitated, the aqueous layer should not show more than a light rose colour, whilst a yellow colouration of the benzene layer indicates aloes. If, however, the aqueous layer is distinctly red, the bulk of the original solution must again be treated with lead acetate, after which 10 c.c. is filtered, freed from lead, divided into two portions, and one of these portions tested with benzene and ammonia as before. When the precipitation of the hydroxymethylanthraquinones is shown to be complete, the other portion of the filtrate is treated with an excess of bromine water, which, in presence of aloin, gives an immediate flocculent precipitate. The main solution is now freed from lead and 10 c.c. portions of the filtrate are tested as follows. One portion is gently heated and shaken with 2-3 grm. of borax (cf. Vol. VII, p. 149) and allowed to stand for 15 minutes, when, in the presence of aloes, a green fluorescence appears. Another 10 c.c. portion is heated with 1 drop of copper sulphate solution and 1 drop of hydrogen peroxide solution (cf. Klunge's test and Léger's test, Vol. VII, pp. 144 and 149-150). In the presence of aloes, a red colouration is obtained which becomes intensified on standing, whilst samples free from aloes become orange-red and do not alter on standing.

<sup>1</sup> G. Mossler, *Pharm. Post.*, 1913, 46, 313, 325.

**Identification of the Different Hydroxymethylanthraquinone Drugs in Admixture with Aloes.**—The alcoholic extract is brought to a strength of 50% of alcohol and filtered. The filtrate is boiled for 30 minutes beneath a reflux condenser with about 5% of sulphuric acid, cooled and filtered, and the alcohol expelled from the filtrate by repeated evaporation with water. The hydroxymethylanthraquinones are precipitated, whilst aloin remains in solution. The precipitate is washed free from acid, dried, boiled with benzene, and the benzene extract shaken with 10% sodium carbonate solution and then with dilute sodium hydroxide solution. The two alkaline extracts are separately acidified with hydrochloric acid, each shaken with 20 c.c. of benzene, and 5 c.c. of each benzene extract is evaporated. The residues are heated with 3–4 drops of acetic acid, and the solutions transferred to glass slips and examined, after 30 minutes, in polarised light. The crystals thus obtained from rhubarb, cascara sagrada, senna, etc., show pronounced differences, as is also the case with crystals obtained by sublimation.

#### **Artemisia Bitters.**

**Estimation of Santonin in Wormseed.**—The following method, due to Fromme, has recently been favourably reported on by C. E. Caspari.<sup>1</sup> The finely powdered wormseed (13 grm.) is macerated with occasional shaking with 130 grm. of chloroform. 102.5 grm. of the liquid (= 10 grm. of the drug) is drawn off and evaporated until the residue weighs only 7 to 8 grm. This residue is mixed with 100 c.c. of 5% barium hydroxide solution and heated on the water-bath until the odour of chloroform has disappeared. The liquid is filtered through a wet filter and the insoluble matter washed twice with 10 c.c. of hot water. The filtrate and washings are acidified with 5 c.c. of 25% hydrochloric acid, heated on the water-bath for a few minutes, cooled and shaken out with 20, 15 and 15 c.c. of chloroform. The extracts are filtered and evaporated to dryness. The residue is dissolved in 7.5 grm. of absolute alcohol and 42.5 grm. of hot distilled water are then added. The milky liquid is filtered immediately into a tared flask and the filter washed twice with 10 grm. of 15% alcohol. After 24 hours, the liquid is filtered through a tared filter, and the flask and filter washed twice with 10 grm. of the dilute alcohol. The flask and filter are finally dried at 100° C. to constant weight, 0.04 grm. being added to the weight of santonin found.

#### **Hops.**

Since the proofs of Vol. VII were passed, Power, Tutin and Rogerson<sup>2</sup> have published an elaborate paper on the Constituents of Hops, and Chapman<sup>3</sup> a short note on the Nitrogenous Constituents of Hops. If the descriptive

<sup>1</sup> *Amer. Pharm. Assoc.*, 1914, 634.

<sup>2</sup> *Trans.*, 1913, 103, 1267.

<sup>3</sup> *Proc. Chem. Soc.*, 1913, 29, 182.

matter, which preceded the instructions given in Vol. VII (pp. 164-175) for the commercial analysis of hops, purported to be exhaustive, it would be necessary now to refer in detail to the above-mentioned papers. As, however, the plan of this work is to exclude descriptive matter except so far as this is necessary to explain the principles on which commercial methods of analysis are based, Chapman's paper, although adding materially to our knowledge, and although the work of an author who has made a special study of hops from both the chemical and technological points of view, needs only to be cited here, pending his promised investigation of the technological significance of the constituents he has isolated.

The question of the treatment that should be accorded to the work of Power and his collaborators presents more difficulty, but the writer feels that a general discussion of their results may well be deferred. Since, however, these authors express the opinion that their results undermine the whole principle on which the current methods for the commercial analysis of hops depend, this claim is criticised at some length in a subsequent paragraph dealing with the Estimation of Soft and Hard Resins. Power and his collaborators have derived from hops a great number of compounds, including minute quantities of two new crystalline, phenolic substances, one of which is bitter, and notable quantities of fatty acids. It is on the latter ground, mainly, that they attack current methods of analysis.

Yet there is no evidence in their paper that hops contain fatty acids as such, or many other of the compounds that they isolated. That fatty esters would be present in an extract of ground Kentish hops would have been expected by anyone conversant with the fact that the seeds of the hop contain upwards of 25% of a fatty oil (Vol. VII, p. 177), and that the hops employed by them were well seeded may be inferred from the fact that the ground sample yielded no less than 21.8% of matters soluble in petroleum ether. The isolation of fatty acids was preceded by saponification with alcoholic potash and it has been known for 10 years that one of the best characterised constituents of the "soft resin" (the so-called  $\alpha$ -acid) yields valeric acid on such treatment, which would also saponify the fatty oil derived from the seeds and not improbably break down other constituents of the resin. It is as remarkable as it is unfortunate that chemists of the unquestioned attainments of Power and his collaborators should have studied—as they appear to have studied—the literature of the subject, without appreciating the extraordinary instability of many of the constituents of the hop, and that they should have embarked on this elaborate research without due regard to this fact. Even before their treatment of the petroleum extract with alcoholic potash, they had probably brought about profound changes in its composition, for they subjected it twice to distillation in a current of steam, once for 5 hours. As Chapman pointed out in the discussion of their paper,<sup>1</sup> the fact that certain of the petroleum-

<sup>1</sup> *Proc. Chem. Soc.*, 1913, 29, 180.

soluble and preservative constituents might be converted, by simply boiling with water, into products insoluble in petroleum and possessed of little or no preservative properties, was not only well known, but was one of the facts that a well-planned study of the constituents of hops would have sought to explain. Enough has been said to show that the painstaking work of Power and his collaborators was not planned in such a way as to throw light on this and cognate questions, and, important as some of their results may ultimately prove, one must agree with Chapman that their immediate practical value is small.

The recent work of Brown and Clubb<sup>1</sup> makes it necessary to correct certain statements in Vol. VII. Applying the method of Brown and Ward (Vol. VII, p. 179), they find that the relation between the antiseptic power of hops and their total content of soft resins is much less simple than was at one time supposed. That the relationship was one of strict proportionality was never held, as it has always been recognised that the soft resin was a mixture in variable proportions of at least four substances, whilst, so long ago as 1901, Barth announced that he had secured direct evidence that one of the constituents was more powerfully antiseptic than another. Nevertheless, there was a general impression, which found support in the practical experience of brewers, that the total content of soft resins was a very fair measure of the antiseptic properties of hops. As evidence of this may be cited the facts that the determination of soft resins was constantly asked for by brewers and carried out by chemists, whereas the method of Brown and Ward received little attention until the appearance of the further paper by Brown and Clubb.

These authors have shown that two samples of hops of equal resin content may differ in antiseptic power in the ratio of 2 : 1 when tested by the direct method of Brown and Ward, and that two samples of hops of equal antiseptic power when tested by that method may differ in soft resin content in the ratio of 2 : 1. This is the approximate order of magnitude of the maximum divergencies observed and is of course serious. At the same time they have shown that the antiseptic power of the  $\alpha$ -acid is about four times as great as that of the  $\beta$ -acid. Barth stated that the  $\beta$ -acid was the more powerful, but he gave no figures, and in 1901 no precise method of measurement was available, so that the result of Brown and Clubb must stand for the moment, although they are careful to say that they were unable to obtain either acid in a crystalline condition. In view of the fact that the crystalline acids are so insoluble that they could hardly function as such in the Brown and Ward process any more than in the brewer's copper, but would first go over into the corresponding resins, the failure of Brown and Clubb to obtain them in crystalline form may be unimportant.

Since it is known that the more powerfully antiseptic  $\alpha$ -resin may con-

<sup>1</sup> *J. Inst. Brewing*, 1913, 19, 261.

stitute anything from 5% to nearly 50% of the total soft resin,<sup>1</sup> it seems probable that a constant relationship may be found to exist between the antiseptic power of hops and  $4A + B$ , where A and B represent the percentages of  $\alpha$ - and  $\beta$ -resins respectively. Brown and Clubb have published no data bearing on this point, but it appears deserving of investigation, as the wide variation in the ratio of  $\alpha$ -resin to total soft resin and the great superiority of the  $\alpha$ -resin as an antiseptic make it possible for two hops of equal soft resin content to differ even more widely in antiseptic power than any pair of examples cited by Brown and Clubb and may afford a complete explanation of their results above referred to.

Other results of Brown and Clubb are less easy of explanation. Chapman cites them<sup>2</sup> as having shown that a period of extraction quite insufficient for the solution or removal of the resins will suffice to extract the substance or substances on which the preservative properties of hops depend. A careful perusal of their paper, however, discloses the fact, not unexpected by one familiar with the praiseworthy care not to overstate his case that characterises all the utterances of A. J. Brown, that the authors do not claim to have proved quite so much as Chapman states. They say—and rightly say—that certain results of theirs do suggest such a conclusion as Chapman draws, but they are careful not to claim that their results amount to a proof, and the writer thinks this a convenient opportunity to point out that other explanations—less subversive of all our earlier views on hops—may possibly be found for their results. What they in fact found was that an aqueous extract of hops, prepared according to the method of Brown and Ward, did not contain more resin than corresponded to 23% of the soft resin in the original hops used. In another experiment, with hops of a different kind, it was found that when these were extracted as directed by Brown and Ward, then reextracted twice more in a similar manner, and the antiseptic powers of the successive extracts compared, these antiseptic powers stood in the ratio of 100:20:8. Combining these results—which may or may not be justified as the hops differed—one gets the suggestion that some constituent of the hop resin may have an antiseptic power 12 times as great as that of the others. Brown and Clubb, however, did not isolate any constituent possessed of such properties, and it is at least possible that their results may be explained without assuming the existence of such a substance. Their own results show that even 1 hour's extraction with water at 100° under their conditions leads to profound changes in the original soft resins, other than those extracted during the process. A portion of these soft resins is converted into hard resin, which would not confer any antiseptic properties on water subsequently boiled with the hops, and this transformation of soft resin into hard resin might be expected to continue during the second and third periods of extraction. Even the

<sup>1</sup> H. V. Tartar and B. Pilkington, *J. Ind. Eng. Chem.*, 1913, 5, 478.

<sup>2</sup> *Analyst*, 1913, 38, 599.

resins remaining soluble in petroleum after this treatment may have undergone a change involving a diminution in their antiseptic power. It is recognised that this attempt to explain Brown and Clubb's results, without resort to the hypothesis of some constituent of far higher antiseptic power than is possessed by any yet isolated, implies the suggestion that an extract prepared in accordance with the directions of Brown and Ward may have only about half the antiseptic power of the hops from which it is prepared, the antiseptic power of the unextracted soft resins, even if consisting wholly of the less toxic  $\beta$ -resin, being largely destroyed by the process of extraction. This, however, does not touch the principle of Brown and Ward's method as a practical test of the brewing value of copper hops, since Brown and Ward's extraction process is not very different from a brewery boil. It also follows, if the writer's suggestion is correct, that only a portion—perhaps less than half—of the preservative constituents of hops finds its way into a brewer's wort, but this has long been suspected. What is not yet known with certainty is whether the practical preservative power can be expressed as a function of the content of  $\alpha$ - and  $\beta$ -resins. That preservative power is not proportional to  $\alpha + \beta$  is amply proved, but that it may be proportional to  $k\alpha + \beta$ , where  $k$  is a constant approximating 4, is suggested as distinctly probable by the work of Brown and Clubb and that of others read in the light of these authors' results.

### Commercial Analysis of Hops.

**Estimation of Soft and Hard Resins.**—Some years ago, Lintner<sup>1</sup> and Siller<sup>2</sup> stated that, unless hops were finely comminuted, petroleum ether failed to extract the soft resins completely, and it has become customary on the Continent to pass hops through a mincing machine<sup>3</sup> before proceeding to the estimation of soft resins. With Continental hops, substantially free from seeds, there is no objection to this fine grinding, but with seeded British or American hops such treatment ruptures the seeds, liberating the fatty oil contained in them (Vol. VII, p. 177) and cannot be resorted to where the soft resins are finally to be estimated by a simple gravimetric method such as that of Briant and Meacham (Vol. VII, p. 175). No objection attaches to fine grinding, even with seeded hops, if the final estimation is made by Lintner's volumetric method (Vol. VII, p. 177), which depends on the acid function of the soft resins.

When the manuscript of Vol. VII was penned, however, Lintner's volumetric method was very little used in Britain, where the method of Briant and Meacham was generally employed. For these reasons, among others, no reference was made in Vol. VII to the then recent German proposals to resort to fine grinding. Such procedure could not be applied to British hops

<sup>1</sup> *Chem. Zeit.*, 1908, 32, 1068.

<sup>2</sup> *Zeitsch. Nahr. Genussm.*, 1909, 18, 241.

<sup>3</sup> D. Neumann, *Wochenschr. f. Brauerei*, 1910, 27, 281.



without abandoning the analytical method in most general use, and at that date there was no evidence that the results obtained by the method of Briant and Meacham were liable to serious error. Such evidence as existed that extraction with petroleum ether was incomplete, unless fine grinding were resorted to, rested on experiments in which the period of extraction was much shorter than the 24 hours directed by Briant and Meacham.

On the Continent, there has always been a tendency to reduce the time of extraction and, when following the directions for extraction given by Lintner in the original description of his volumetric method (Vol. VII, p. 177), this appears to be permissible. An objection to that method, that has tended to restrict its use here, is the large volume of petroleum ether required (500 c.c.), but the use of a large volume of solvent maintained with the hops at 50° C. does make it possible to reduce the time of extraction materially below that required when a Soxhlet extractor is used. A few experiments by the writer confirmed Lintner's claim that 8 hours was sufficient, but it is possible that with some hops extraction would be incomplete. When using a Soxhlet extractor, the error attending a reduction of the period of extraction varies according to the sample, but with some samples is large. Since 1908 or thereabouts, the inconvenience attending the use of large quantities of solvent appears to have led German chemists to return to the use of a Soxhlet extractor. Siller (*loc. cit.*) makes mention of the use of a Soxhlet apparatus and, since he extracted for only 10 hours, his discovery that unground hops could not be completely extracted in this time accords with British experience and does not appear to touch the principle of Briant and Meacham's method.

More recently, however, this method has been seriously impugned by Tartar and Bradley.<sup>1</sup> These writers show a more intimate acquaintance with the work of others than is usual among writers on hops, and it must be assumed that the method they condemn as giving low results is the unamended method of Briant and Meacham, including the 24 hours' period of extraction. They say that the method of Briant and Meacham gives very much lower results for soft resins, and correspondingly high ones for hard resins, than does the latest form of Lintner's volumetric method or a new gravimetric method now described by them. In one case the latter methods discovered 16% of soft resin, whereas the process of Briant and Meacham is said to have extracted only 8%. The results of Lintner's original method are said to be in good agreement with those obtained by the method of Briant and Meacham, but both methods are said to fail because, without previous grinding, the whole of the soft resin cannot be extracted by petroleum ether.

Tartar and Bradley (*loc. cit.*) have devised a new gravimetric method which can be applied even to finely ground, seeded hops. They claim, prob-

<sup>1</sup> *J. Ind. Eng. Chem.*, 1912, 4, 209.



ably with justice, that their method is the most exact yet available, but it will not be described here as it is very tedious and as its authors themselves express the opinion that Lintner's modified volumetric method (described below) is the best method for commercial purposes, since it is rapid and yields results which seldom differ by more than a few tenths of 1% from those yielded by their own exact method.

**Lintner's Modified Volumetric Method for the Estimation of Soft Resins** differs from that described under his name in Vol. VII, p. 177 only in that the hops are first put through a mincing machine, the first portions being rejected, and are then extracted in a Soxhlet extractor for 8-10 hours with a minimum quantity of petroleum ether at the comparatively low temperature determined by this method of extraction, instead of at 50° C. in a flask with 300 c.c. of petroleum ether. That on one and the same extract, prepared from uncrushed hops, Lintner's titration method gives substantially the same results as evaporation of the extract as directed by Briant and Meacham has long been known. That Briant and Meacham's method cannot be applied to crushed hops is obvious, whereas Tartar and Bradley have shown conclusively that no such objection attaches to Lintner's titration method. If Tartar and Bradley are also right in stating that the method of Briant and Meacham may give low results owing to incomplete extraction, the modified Lintner method stands out as the simplest method by which the soft resins can be estimated accurately.

The writer thinks it right to state that he has been unable to confirm Tartar and Bradley's observation that Briant and Meacham's method may lead to substantial error, and the continued use of that method in well-informed circles in Britain suggests that the explanation of Tartar and Bradley's results may possibly lie in some experimental detail hitherto not recognised as important. On the other hand, the writer's own experiments to elucidate the point were few in number and a great deal of negative evidence would be necessary to outweigh the definite finding of Tartar and Bradley. In view of the facts that grinding makes it possible to complete the extraction in 8 hours instead of 24, without the use of inconvenient quantities of solvent, and that such grinding of British hops renders Briant and Meacham's method inaccurate, Lintner's modified method has now much to recommend it, even if further experiment should free Briant and Meacham's method from the aspersions cast on it by Tartar and Bradley.

A more general use of Lintner's improved method may therefore be expected and, in the writer's opinion, the results hitherto published by Power, Tutin and Rogerson are insufficient to provoke a contrary result. These authors have stated<sup>1</sup> that "such methods for the valuation of hops as are based on the titration of extracts obtained by means of light petroleum and similar solvents are of very doubtful utility" because "the resinous material contains a large proportion of fatty acids and their esters." This criticism,

<sup>1</sup> *Trans.*, 1913, 103, 1292.

if sound, would apply to the gravimetric method of Briant and Meacham no less than to the volumetric method of Lintner, and, since Power and his collaborators offer us nothing in place of these methods, would leave us without any chemical method of estimating the preservative value of hops. On pages 550 to 552 the work of Power and his collaborators, which covers many substances beyond the bitters and resins of hops, is briefly referred to, and grounds are there stated for regarding as far from complete their alleged proof that an ordinary petroleum ether extract of hops contains notable amounts of fatty acids. That the "soft resins" of hops, as ordinarily obtained, were a mixture of at least two resins and two crystalline acids, together with traces of essential oil and wax, was generally recognised, but, as Chapman pointed out<sup>1</sup> in discussing the paper of Power and his collaborators, the analytical methods which they regarded as of very doubtful utility had in fact done very good service from the technical point of view. Among German critics of Power, Tutin and Rogerson may be cited O. Neumann,<sup>2</sup> who states that their conclusions are contrary to established experience, which leaves no doubt as to the utility of the methods they condemn. The writer need do no more than state that, so far as he can learn, these methods remain in general use.

That in future less reliance must be placed on the single figure for total soft resins as a measure of the value of hops, and that much more general use ought to be made of Lintner's method of discriminating between the  $\alpha$ - and  $\beta$ -resins (Vol. VII, pp. 177-178) follows from the work of Brown and Clubb, referred to on pages 552 to 554. If sufficient workers could be found to make such an extended chemical analysis and at the same time to make use of the biological method of Brown and Ward for the direct estimation of preservative power, it might well be that some simple expression would be found to correlate the chemical and biological results. In such an event, the biological method might be expected to supersede chemical methods in brewing laboratories, since it requires less time, whilst chemical methods would no doubt be preferred by those only occasionally concerned with hop analysis, owing to the inconvenience of maintaining cultures of *Bacterium X* and culture media over long periods.

**Direct Estimation of the Antiseptic Power of Hops.**—Comparatively little progress has been made towards a general adoption of the method of Brown and Ward, outlined on pages 179-181 of Vol. VII. The method, however, assumes greatly increased importance since the publication of the work of Brown and Clubb (pages 552 to 554). Still greater importance may attach to it if Power and his collaborators should, as a result of further research, justify the aspersions they have cast on all the chemical methods of valuing hops.

It was pointed out in Vol. VII that, before the method of Brown and

<sup>1</sup> *Proc. Chem. Soc.*, 1913, 29, 181.

<sup>2</sup> *Chem. Zeit.*, 1913, 37, 1317.

Ward could pass into general use, it would need to be approximated to the Rideal-Walker method of testing disinfectants by using as standard a solution of some antiseptic of definite composition. Brown and Clubb have since published data<sup>1</sup> which show that salicylic acid would serve for this purpose and, in discussing their paper, the writer<sup>2</sup> made some definite suggestions for expressing all results in terms of salicylic acid. The *Journal of the Institute of Brewing* should be watched for further developments of the method of Brown and his collaborators, but meanwhile reference to the paper of Brown and Clubb (*loc. cit.*) and to the discussion thereon will enable anyone to use the method and to express his results in such a way that they will be comparable with those of other workers and convertible into terms of any standard that may ultimately be agreed upon. The writer's contribution to the discussion was made without a full knowledge of Brown and Clubb's results and under the supposition that the  $\beta$ -resin was more toxic than the  $\alpha$ -resin. As described in the preceding paragraphs, Brown and Clubb have shown that the  $\alpha$ -resin is the more toxic, but this in no way affects the writer's suggestions for standardising the method of Brown and Ward.

**Estimation of the Bitterness of Hops.**—Since the above was written, a paper<sup>3</sup> has appeared entitled the Quantitative Determination of the Resins in Hops. Although possessing the authority which must attach to any paper issuing from the Carlsberg Laboratory, the writer prefers to introduce it under the above heading, as the method does not measure the total content of resins, nor that of soft resins. Evidence is, however, adduced that it affords an approximate measure of the bitterness of hops. It is an expeditious method, consisting essentially in extracting the total resins with cold ether and titrating the extract with alcoholic potash. It assumes that the hard resin is bitter—a fact the authors claim to have proved—but less bitter than the soft resins, a fact which is compensated in this method by its much greater equivalent. The method is as follows:

The hops are put through a mincing machine and 5 gm. are transferred to a 300 c.c. flask and dried in a vacuum for 24 hours at 35° C. The dried material is then covered with 150 c.c. of absolute ether and left for 1 hour with repeated shaking. The liquid is then filtered and the residue washed with 100 c.c. of ether. Finally the filtrate is titrated with *N*/20 alcoholic (93%) potassium hydroxide, using 6 to 8 drops of 1% phenolphthalein as indicator, the titration being continued until further additions of alkali no longer increase the colour intensity. Each c.c. of *N*/20 potassium hydroxide corresponds to 0.02 gm. resin. This factor is only exact for the  $\beta$ -resin; the  $\gamma$ -resin has a much higher equivalent, but, as the bitterness of the resins is approximately proportional to the reciprocals of their equivalents, the use of this factor approximately measures the bitterness of the hops. The previous drying and the use of

<sup>1</sup> *J. Inst. Brewing*, 1913, 19, 272-274.

<sup>2</sup> *Ibid.*, 290.

<sup>3</sup> O. Winge and J. P. H. Jensen, *Compt. rend. du Lab. de Carlsberg*, 1914, 11, 116.

absolute ether are essential, as otherwise tannins pass into solution and introduce errors. Even with hops containing so little as 4.5% of water and with absolute ether, the resins may be overestimated by 1% (on the hops).

The above-quoted paper criticises adversely all previous methods for the valuation of hops, especially such as depend on differentiation of the hard and soft resins. The authors' discovery that the hard resin does confer a bitter flavour on liquids boiled with it is the basis of this criticism, but they seem to overlook the fact that British workers at least have been more concerned to measure the preservative properties than the bittering properties of hops. So far as the writer is aware, there is no evidence that the hard resin has any preservative value. Nor does he know of any evidence for the authors' statement that the resin produced by the oxidation and polymerisation of hop oil is identical with the  $\gamma$ -resin. Hayduck, it is true, expressed this view in 1888, but he adduced no evidence, and such as has accumulated since leads to a contrary conclusion.

**Estimation of Arsenic in Hops.**—In Vol. VII, p. 186, directions were given for the destruction of organic matter as a preliminary to the estimation of arsenic, and it was stated that if this were omitted, arsenic might be underestimated. In reviewing Vol. VII, A. C. Chapman<sup>1</sup> stated that, in his experience, higher results were, as a rule, obtained when working directly on the hops than when the organic matter was destroyed. The writer takes this opportunity of stating that his personal experience accords with that of Chapman. Having tried every method for the destruction of organic matter which he has seen recommended, he has never recovered more arsenic after such treatment than when it was omitted, and sometimes he has found less, but in writing for Vol. VII he did not feel justified in giving his own view which he knew conflicted with the experience of many chemists constantly occupied with the examination of brewing materials.

<sup>1</sup> *Analyst*, 1913, 38, 599.

# ANIMAL BASES.

By K. GEORGE FALK, PH.D.

**Ninhydrin Test.**—The conditions for carrying out the triketohydrindene hydrate,  $C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} C(OH)_2$ , (*ninhydrin*<sup>1</sup>) test for the presence of amino-

acids, peptides, peptones, proteins, etc., have been studied in detail.<sup>2</sup> In carrying out this test, 2–10 c.c. of the solution in question are boiled for 1 minute with 0.2 c.c. of a 1% aqueous triketohydrindene hydrate solution. The appearance of a blue colour shows the presence of a substance containing a carboxyl and an amino-group attached to an aliphatic radical. Certain precautions are necessary. The solutions must be neutral. A blue colouration will appear if a strongly alkaline ninhydrin solution is warmed but this colour disappears on dilution. Since the coloured substance obtained is colloidal and sensitive towards electrolytes (cations exerting the predominating action), only small amounts of neutral salts may be present. The test is given most readily if the amino-group is in the  $\alpha$  position to the carboxyl group; if it is in the  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ , positions, the blue colour appears only on heating. Fairly concentrated solutions of alcohols, aldehydes, ketones, and reducing sugars give a red or blue colouration when warmed with a ninhydrin solution; the colour is intensified by the addition of alkali and is said to be different from that obtained with amino-acids, etc. Addition of alkali to the test with the latter after the colour has developed, does not dissipate the colour. The reagent is sensitive for the following substances in the dilutions indicated: Glycocoll, 1:65,000; *d*-alanine, 1:26,000; *d*-valine, 1:15,000; *L*-leucine, 1:25,000; *d*-glutamic acid, 1:22,000; asparagine, 1:19,000; *dl*-phenylalanine, 1:26,000; *L*-histidine, 1:79,000;  $\alpha$ -aminobutyric acid 1:16,000.

**van Slyke Apparatus.**—The apparatus devised by van Slyke for quantitatively estimating amino-groups by the reaction with nitrous acid and measurement of the nitrogen evolved has been improved in a number of particulars. For shaking the deaminising bulb and the Hempel pipette a motor is used. The apparatus is constructed with rubber connections and outflow tubes so that now it can be used an indefinite number of times without disconnecting any of its parts.<sup>3</sup> The mechanical shaking device increases the convenience, speed, and reliability of the results. To prevent foaming of viscous solutions

<sup>1</sup> Put on the market by Meister Lucius and Brüning, Höchst a.M.

<sup>2</sup> Paul E. Howe, *Biochem. Bulletin*, 1914, 3, 269; Abderhalden and Schmidt, *Z. physiol. chem.* 85, 143; E. Herzfeld, *Biochem. Zeit.*, 59, 249; Halle, Loewenstein and Pribram, *Ibid.*, 55, 357.

<sup>3</sup> It may be obtained with or without motor from Emil Greiner, 45 Cliff St., New York, or from Robert Goetze, 4 Hörtelstrasse, Leipzig. In England it is made by Müller, Orme & Co.

during the shaking, the addition of caprylic alcohol (Kahlbaum's "octyl alcohol (secundär)I") is recommended in place of the amyl alcohol originally suggested. A useful table for the conversion of c.c. of nitrogen gas into milligrams of amino-nitrogen at various temperatures and pressures is appended to this paper.<sup>1</sup> In a later paper<sup>2</sup> van Slyke describes a micro-form of this apparatus which answers almost all the requirements of ordinary work. The gas burette in this form holds 10 c.c., the upper part measuring the first 2 c.c. is 4 mm. in diameter and is divided into divisions of 0.02 c.c., the remainder is wider and divided into 0.05 c.c. The deaminising bulb has a volume of 11 to 12 c.c., and the burette of 2 c.c. 10 c.c. of nitrite solution and 2.5 c.c. acetic acid are required for each analysis and the correction for the reagents is 0.06–0.12 c.c. Only 0.5 mg. of amino-nitrogen is required for an analysis accurate to within 1%. The manipulations are the same as with the larger apparatus except that in the first stage of the analysis in freeing the apparatus from air the deaminising bulb should be shaken by the motor at a very high speed about as fast as the eye can follow. In the third stage when the nitric oxide is absorbed by the permanganate, the Hempel pipette should be shaken not faster than twice per second.

**Sørensen's Formaldehyde Method.**—The estimation of amino-acid nitrogen in fluids such as urine by the Sørensen formaldehyde method (titration with alkali after addition of neutralised formaldehyde solution) has been modified by using phosphotungstic acid to remove ammonia and other impurities.<sup>3</sup> The method is as follows: 200 c.c. of urine (24 hours' specimen diluted to 2,000 c.c.) are measured into a 500 c.c. Erlenmeyer flask, an equal quantity of 10% phosphotungstic acid (Merck's) in 2% hydrochloric acid added, allowed to stand at least 3 hours, 250 c.c. clear liquid decanted, 1 c.c. of a 0.5% phenolphthaleïn solution added, and then barium hydroxide a little at a time until the whole fluid turns decidedly pink. The mixture is allowed to stand 1 hour, two 100 c.c. samples (= 50 c.c. urine) are filtered off, neutralised to litmus with *N*/5 hydrochloric acid, 10–20 c.c. of neutralised formaldehyde solution added, and titrated to a deep red colour. The result is corrected by deducting the amount of *N*/10 sodium hydroxide necessary to produce the same depth of colour in an equal quantity of water, freed from carbon dioxide, to which the same quantity of neutral formaldehyde has been added.

**Esterification Method.**—The separation of amino-acids by Fischer's ester method is not quantitative, as is well known. Loss occurs at each operation—esterification, distillation, and saponification. Some evidence has been obtained as to the percentage loss under the best conditions of alkali, etc., by experienced workers, starting with pure amino-acids. The percentage yields obtained after carrying through the three operations were as follows:

<sup>1</sup> *J. Biol. Chem.*, 1912, 12, 275.

<sup>2</sup> *J. Biol. Chem.*, 1913, 16, 122.

<sup>3</sup> S. R. Benedict and J. R. Murlin, *J. Biol. Chem.*, 1913, 16, 385.

<sup>4</sup> Abderhalden and Weil, *Z. physiol. Chem.*, 77, 59; Osborne and Jones, *Am. J. Physiol.*, 26, 212.



glycocoll 65%; *d*-alanine 64%; *l*-leucine 75% (in another case 88.8%); *d*-valine 68%; *l*-phenylalanine 54%; *l*-proline 69.5%; aspartic acid, about 60%; glutamic acid, about 70% (in another case 85%). In the hydrolysed protein material, which is separated by fractional distillation of the esters, it has been suggested that the fraction which formerly was distilled above 110° at less than 1 mm. pressure be worked up directly without distillation, this fraction being dealt with as easily in this way as by the old method.<sup>1</sup> The results of amino-acid distillations compared with the figures obtained by the hydrolysis of proteins indicate that most, if not all, of the fragments of the more common proteins have already been isolated, the losses being accounted for in the different manipulations.

**Amino-acid Picrolonates.**—The picrolonates of a number of amino-acids have been prepared.<sup>2</sup> They may be obtained by dissolving molecular proportions of amino-acid and picrolonic acid in a small amount of warm water and allowing to crystallise. Many of them are insoluble in cold water but much more readily soluble in alcohol. The following list gives the solubility of the picrolonates of the corresponding amino-acids in grm. per 100 c.c. of water at 20°–23°, and also the melting points: *dl*-phenylalanine, 0.12, 212° (decomp.); tyrosine, 0.29, blackens at 260°; *l*-phenylalanine, 0.34, 208°; *dl*-leucine, 0.53, indefinite above 140°; *l*-leucine, 0.55, indefinite at about 150°; *d*-isoleucine, 0.58, 170°; *dl*-valine, 0.81, indefinite above 150°; *dl*-serine, 0.98, decomposes 265°; glycine, 0.99, 214°; *dl*-alanine, 1.01, 216°; *d*-valine, 1.20, 180°; *d*-alanine, 1.61, 214°; *dl*-aspartic acid, 1.69, blackens at 130°; *dl*-glutamic acid, 2.37, 194°. Proline and oxyproline do not yield picrolonates readily under these conditions. Separations may be effected with these salts; for instance, phenylalanine can be separated from glutamic and aspartic acids by adding enough picrolonic acid to combine with the former, when its picrolonate will crystallise out pure.

**Separation of *d*-Valine and *d*-Alanine.**—The ester method of separating amino-acids obtained from protein hydrolysis gives, by distillation and crystallisation, a number of fractions and subfractions containing two or more amino-acids which are difficult to separate in the ordinary way. A method for separating *d*-alanine (and glycine, if present) and *d*-valine, which are obtained in one of these fractions, has been devised by Levene and van Slyke.<sup>3</sup> The method is based on the fact that a crystalline salt is formed by *d*-alanine with phosphotungstic acid in a ratio of 1 to 14 by weight and solubility 0.15 grm. alanine per 100 c.c. in a solution containing 20 grm. phosphotungstic acid in 100 c.c. 10% sulphuric acid, while under the same conditions the solubility of *d*-valine is 1.21 grm. per 100 c.c. By alternate crystallisation of valine as the free amino-acid (with the addition of acetone to a concentration of 50–60%), and of alanine as the phosphotungstate, subsequently remov-

<sup>1</sup> Osborne and Jones, *loc. cit.*

<sup>2</sup> Levene and van Slyke, *Proc. Soc. Exp. Biol. Med.*, 9, 111

<sup>3</sup> *J. Biol. Chem.*, 1913, 16, 103.



ing the phosphotungstic acid with lead acetate, a practically quantitative separation of a mixture of the two amino-acids can be effected.

**Separation of Cystine and Tyrosine.**—A method has been devised<sup>1</sup> for separating cystine and tyrosine from each other (see Vol. VIII, Appendix, p. 689). The mixture is warmed with absolute alcohol saturated with hydrochloric acid and an equal volume of alcohol then added. Cystine is insoluble and may be filtered off, washed, dried, and weighed. Tyrosine readily forms the ester under these conditions and goes into solution. It may be recovered by diluting with 2 volumes of water, boiling for 8 hours and neutralising with ammonia.

**Tyrosine.**—Tyrosine in the free condition or in peptide combination may be estimated colourimetrically as follows:<sup>2</sup>

1 grm. of the dry protein is accurately weighed out and transferred to a 500 c.c. Kjeldahl flask, 25 c.c. of 20% hydrochloric acid are then added, the flask closed by means of a Hopkins condenser made from a large test-tube, and the contents of the flask boiled for 12 hours over a microburner. At the end of this time the flame is removed, the contents of the flask transferred on cooling to a 100 c.c. volumetric flask and made up to volume. 1 or 2 c.c. of this solution are then transferred to a 100 c.c. volumetric flask, 5 c.c. of the tyrosine reagent<sup>3</sup> added, and after 5 minutes 25 c.c. of a saturated solution of sodium carbonate, and the mixture then made up to 100 c.c. with cold tap water. The maximum colour (blue) develops in about 10 minutes. Therefore the reading should not be made before this time has elapsed. Fading is very slow in the presence of the large excess of reagent used. As nearly at the same time as possible a standard is prepared by treating 1 mg. of pure tyrosine with 5 c.c. of the phosphotungstic-phosphomolybdic reagent, then adding 25 c.c. of saturated sodium carbonate solution and making up to volume. The colours are compared by means of a Duboscq colourimeter, the standard solution being placed at 20 mm. As a standard solution, a solution of pure tyrosine in *N*/10 hydrochloric acid is used of such a concentration that 5 c.c. contain 1 mg. of tyrosine. In making the comparison of colour both solutions should of course be absolutely clear and contain no trace of precipitate; if any cloudiness is observed the solution should be filtered before being used.

Tryptophane and hydroxytryptophane also have been observed to give a slowly developing blue colour with this reagent.<sup>4</sup>

**Tryptophane.**—A quantitative method has been proposed for tryptophane based upon the blue colour developed slowly (30 hours) with a solution containing 20 grm. of *p*-dimethylaminobenzaldehyde, 500 c.c. concentrated hydrochloric acid, and 500 c.c. water. For colour comparison, an ammoniacal copper sulphate solution is used.<sup>5</sup> It is said that 0.1 mg. of tryptophane may be determined in 100 c.c. solution in this way.

**Betaine.**—A new process of obtaining betaine hydrochloride from molasses residues was described by Stoltzenberg.<sup>6</sup> It depends upon the changes

<sup>1</sup> Plimmer, *Biochem. J.*, 1913, 7, 311.

<sup>2</sup> Polin and Denis, *J. Biol. Chem.*, 12, 245; 14, 457.

<sup>3</sup> A solution containing 10 % of sodium tungstate, 2 % of phosphomolybdic acid and 10 % of phosphoric acid is made up by adding 100 grm. of sodium tungstate, 20 grm. of phosphomolybdic acid, and 50 c.c. of 85% phosphoric acid to 750 grm. water, boiling for 2 hours with a reflux condenser, cooling, and diluting to 1000 c.c.

<sup>4</sup> Abderhalden, *J. Biol. Chem.*, 15, 357; *Z. physiol. Chem.*, 83, 468; 85, 91.

<sup>5</sup> Herzfeld, *Biochem. Zeit.*, 1913, 56, 258.

<sup>6</sup> *Ber.*, 1912, 45, 2248.

in solubility produced by saturating solutions with hydrochloric acid; the solubility of potassium chloride decreases from 34 to 1.9 parts per 100 at 20°, that of glutamic acid hydrochloride from 38 to 1.4, whilst that of betaine hydrochloride increases from 40 to 41 parts. In a mixture of the three, the latter has a salting out effect on the other two.

**Urea.**—The quantitative estimation of urea may be carried out very readily by means of soja beans. The latter contain a urease which converts quantitatively the urea into carbon dioxide and ammonia (compare footnote, Vol. VII, p. 300). The estimation of the ammonia may then be carried out in the usual way, either by distillation into standard acid or by direct titration with a suitable indicator (methyl-orange). The method employed by Plimmer and Skelton<sup>1</sup> for the quantitative estimation of urea, and indirectly of allantoin, in urine is the simplest and easiest to carry out. It may best be described in their own words: "In its simplest features the method is no more than Folin's method<sup>2</sup> of estimating ammonia in urine. By fitting together three or four cylinders and Allihn bottles in series with a sulphuric acid bottle at the end, duplicate estimations of ammonia and urea in urine can be carried out simultaneously. In the cylinders for the urea estimations are put 50 to 60 c.c. of water, 1 grm. of finely ground soja beans and 5 (or 10) c.c. of urine. These cylinders are kept in a water-bath at a temperature of 35°–40° and an air current is drawn through the series. After about an hour the rubber connections between the cylinders and bottles are disjointed and 1 grm. of anhydrous sodium carbonate is dropped into the cylinders; they are then connected together again and the air current drawn through for another hour. To prevent frothing, liquid paraffin B. P. has been used; it is superior to petroleum and toluene as it does not evaporate and it obviates the necessity of using a tube containing cotton wool between the cylinder and Allihn bottle. It is not necessary to carry out a blank experiment with soja bean alone, since no ammonia was evolved by two different samples of the bean which were tested several times. The Allihn bottles are charged with excess of *N*/10 sulphuric acid (25 or 50 c.c.) which is titrated with *N*/10 alkali, using Alizarin Red as indicator. . . .

"Not only urea, but also allantoin, is decomposed by the magnesium chloride method of Folin. . . . Since urease has no action upon allantoin, the two substances can therefore be readily estimated in urines which contain both compounds; the difference between the two data will give the amount of allantoin."

The estimation of urea in other fluids may be carried out similarly. Several different methods have been described for the estimation of urea by means of the soja bean urease (E. K. Marshall, Jr., van Slyke, etc.), all based upon the same principle and differing only in some of the manipula-

<sup>1</sup> *Biochem. J.*, 1914, 8, 70.

<sup>2</sup> *Z. physiol. Chem.*, 37, 161.

tions. Solid preparations from soja beans containing the active enzyme are on the market under the names of Arlco-urease and Urease-Dunning. The specific character of the soja bean urease also makes it a convenient reagent for getting rid of urea as such in solutions which are to be used for other purposes. At the present time it appears as though this method of estimating urea is replacing the former methods.

**Creatine; Creatinine.**—The preparation of creatine and creatinine from urine in considerable quantities can now be carried out by the process developed by Benedict.<sup>1</sup> The method is as follows: To each 1,000 c.c. of urine (which must not be decomposed) 18 gm. of picric acid are added. It does not pay to work with less than 10 litres of urine. The picric acid is dissolved in boiling alcohol (40 gm. to 100 c.c.) and the hot solution is added with stirring. The mixture is allowed to stand over night and the supernatant fluid is siphoned off. The residue is poured upon a large Buchner funnel, drained by suction and washed once or twice with cold saturated picric acid solution and sucked dry. The dry, or nearly dry, picrate is treated in a large mortar or evaporating dish with enough concentrated hydrochloric acid to form a moderately thin paste (about 60 c.c. of acid for each 100 gm. picrate), and the mixture thoroughly stirred with a pestle for 3 to 5 minutes. The mixture is then filtered by suction on a hardened paper, the residue washed twice with enough water to cover it, and sucked as nearly dry as possible each time. The filtrate is at once transferred to a large flask and neutralised with an excess of solid magnesium oxide added in small portions, cooling the flask under running water. When all the hydrochloric acid has been neutralised the mixture will turn bright lemon yellow, or litmus paper may be used to test it. The mixture is then filtered by suction and the residue washed twice with water. The filtrate is at once strongly acidified with a few c.c. of glacial acetic acid, and (paying no attention to a precipitate which may form at this point) the solution is diluted with about 4 volumes of 95% alcohol and filtered by suction any time more than 15 minutes after a slight precipitate (chiefly calcium sulphate) has formed. The final filtrate is treated with 30% zinc chloride solution, using 3-4 c.c. for each 1000 c.c. of urine originally used. This mixture is stirred (a precipitate should form almost immediately) and allowed to stand overnight in a cool place. The supernatant fluid is then poured off and the precipitated creatinine zinc chloride collected on a Buchner funnel, washed once with water, then thoroughly with 50% alcohol, and finally with 95% alcohol and dried. The product should be a nearly white, light crystalline powder. 90 to 95% of the creatinine originally present should be recovered. Ordinarily 1.5 to 1.8 gm. of the double salt should be obtained per 1000 c.c. of urine used. To prepare creatine from the double salt, 100 gm. of the latter are treated with 700 c.c. of water in a large casserole and heated to boiling. 150 gm. of pure calcium hydroxide are then added

<sup>1</sup> *J. Biol. Chem.*, 1914, 18, 183.

with stirring and the mixture boiled gently for 20 minutes (with occasional stirring). The hot mixture is filtered by suction and the residue washed with hot water. The filtrate is treated with hydrogen sulphide gas for a few minutes and poured through a folded filter to remove the zinc. The filtrate is acidified with about 5 c.c. of glacial acetic acid and boiled down rapidly to a volume of about 200 c.c. This solution is allowed to stand overnight in a cool place. The crystallised creatine is filtered off with suction, washed with a very little cold water, and then thoroughly with alcohol and dried. (The filtrate obtained at this point should be diluted with alcohol and treated with zinc chloride (50 c.c. of a 30% solution) for the recovery of unconverted creatinine.) This product is recrystallised by dissolving in about seven times its weight of boiling water, allowing the solution to cool slowly and then to stand for some hours. The crystallised product should be filtered off, washed with alcohol and ether and dried in the air for about half an hour. Thus obtained, the creatine contains water of crystallisation which it loses very readily upon exposure to air. To prepare creatine which can be weighed with exactness, it is necessary to dehydrate this product by heating for some hours at about 95°. The yield in this process is about 18 gm. of recrystallised creatine and about 55 gm. recovered creatinine zinc chloride. To prepare pure creatinine from the double salt, the latter, finely powdered, is placed in a dry flask and treated with seven times its weight (by volume) of concentrated aqueous ammonia. The mixture is warmed slightly and gently agitated until a clear solution is obtained, care being taken to drive off no more ammonia during the warming than is necessary to obtain a clear solution. The flask is stoppered, cooled, and placed in an ice-box for an hour or more. Pure creatinine crystallises out. The yield is 60–80% of the theoretical. If the product is coloured slightly yellow, it may be recrystallised either from boiling alcohol or by dissolving in five times its weight (by volume) of concentrated ammonia (warming enough to effect solution) and letting the solution stand in a cold place for some hours. Recrystallisation is usually unnecessary.

For the quantitative estimation of creatinine by Folin's method (yellow colour with picric acid and alkali), it is now recommended to replace the bichromate solution used as standard by a standard creatinine solution.<sup>1</sup> The creatinine-zinc chloride double salt may be used and is obtained pure by three recrystallisations from 10 parts of boiling 25% acetic acid and addition of 1 part concentrated alcoholic zinc chloride solution and 1.5 parts alcohol. 1.6106 gm. of the double salt dissolved in 1000 c.c. of *N*/10 hydrochloric acid gives a solution containing 1 mg. creatinine per c.c. Folin has given detailed directions<sup>2</sup> to carry out the estimation of creatine and creatinine in urine, blood, milk, tissues, muscles, etc. For blood or milk the method is as follows: 10 c.c. of the fluid are placed in a 50 c.c. glass-stoppered shaking

<sup>1</sup> Folin, *J. Biol. Chem.*, 1914, 17, 463.

<sup>2</sup> *J. Biol. Chem.*, 1914, 17, 469, 473.

**Cylinder**, filled to the mark with saturated picric acid solution and shaken a few times. About 1 grm. of dry picric acid is added and the mixture shaken for 5 minutes, transferred to centrifuge tubes, the sediment and precipitate shaken down and the supernatant fluid poured through a filter. (If enough substance is available, the quantities taken may be doubled and filtered without preliminary centrifuging.) Proteins are removed by this treatment and the creatine and creatinine obtained in the filtrate. The standard solution to be used contains 0.2 mg. creatinine per 100 c.c.; it is prepared by diluting the standard solution described above with saturated picric acid solution. 5 c.c. of 10% sodium hydroxide solution are added to both the unknown solution and 100 c.c. of the standard solution; the solutions are allowed to stand 10 minutes and compared in a Duboscq colourimeter. Neither solution may contain more than  $1\frac{1}{2}$  times as much creatinine as the other, otherwise the comparisons of colour are not reliable. In collecting blood for this determination, 10 drops of a 20% potassium oxalate solution are sufficient to prevent clotting in 30 c.c. of blood. To estimate both creatine and creatinine in blood or milk, 10 c.c. of the filtrate from 10 c.c. of blood and picric acid solution are heated in an autoclave at  $120^{\circ}$  for 20 minutes in a flask covered with tin-foil, cooled, diluted to 25 c.c. with saturated picric acid solution, 1.25 c.c. of 10% sodium hydroxide solution added and the colour compared with standard solutions containing 0.5, 1 and 2 mg. of creatinine in 100 c.c. saturated picric acid solution, to 20 c.c. of each of which 1 c.c. of 10% sodium hydroxide solution had been added. With the standard set at 10 mm.,

$$\frac{10 \times 125 \times 0.5 \text{ (or 1 or 2)}}{\text{reading of unknown}} = \text{mg. creatine plus creatinine in 100 c.c. blood or milk.}$$

For the estimation of creatine and creatinine in the other substances, similar methods are employed with slight modifications in the procedure depending upon the properties of the material. For creatine plus creatinine in urine, a convenient method is the following (Benedict<sup>1</sup>): Such a volume of urine as will contain between 7 and 12 mg. of total creatinine is introduced into a small flask or beaker and from 10 to 20 c.c. of *N*-hydrochloric acid added together with a pinch or two of powdered or granulated lead. The mixture is boiled over a free flame as slowly or as rapidly as may be desired until very nearly down to dryness, when the heating should be continued to dryness either on the water-bath or holding the vessel and heating carefully for a moment or two. The residue should best stand on the water-bath for a few minutes until most of the excess of hydrogen chloride has been expelled, after which it is dissolved in about 10 c.c. of hot water and the solution rinsed quantitatively through a plug of cotton or glass-wool (to remove all metallic lead) into a 500 c.c. volumetric flask. 20–25 c.c. of saturated picric acid solution are added and about 7–8 c.c. of 10%

<sup>1</sup> *J. Biol. Chem.*, 1914, 18, 192.

sodium hydroxide solution which contains 5% Rochelle salt (to prevent any formation of turbidity, due to dissolved lead—it has no effect upon the creatinine readings). The flask is filled to the mark at the end of 5 minutes and the colour comparisons made as usual. For creatinine in urine (Folin) 1 c.c. of the standard solution is measured into a 100 c.c. volumetric flask, 1 c.c. of urine into another, 20 c.c. of saturated picric acid added to each and then 1.5 c.c. of 10% sodium hydroxide solution. After 10 minutes the flasks are filled to the mark and the colour of the solutions compared. The special 1 c.c. pipettes, accurate to 0.1%, may be obtained from Eimer and Amend, New York. In estimating creatinine in urine, the colour due to sugar and picric acid appears too slowly to interfere, especially in the cold.  $\beta$ -hydroxybutyric acid, at least in the amounts ordinarily present, does not interfere. Acetone and acetoacetic acid interfere markedly and must be removed; acetone by aeration, acetoacetic acid by extraction with ether and subsequent aeration, or by distillation *in vacuo* at temperatures below 65° in the presence of some phosphoric acid.<sup>1</sup> For creatine plus creatinine in diabetic urines, the autoclave method or evaporation to dryness cannot be used; Folin's original method of heating on the water-bath during 3–4 hours with hydrochloric acid is the only safe process; a little evaporation should be permitted to remove the acetone.

To estimate creatine and creatinine in muscle or other tissues, a preliminary treatment with picric acid solution removes the protein substances as insoluble picrates.

**Adenine.**—A method of obtaining adenine from molasses residues has been described by K. Andrlik.<sup>2</sup> They are treated with copper sulphate and sodium hydroxide, the precipitate obtained being decomposed in suspension with hydrogen sulphide and filtered. The filtrate upon evaporation gives crystals of adenine which may be purified by recrystallisation (animal charcoal). 20 grm. of adenine were obtained from 40 kilos of molasses residues.

<sup>1</sup> Greenwald, *J. Biol. Chem.*, 1913, 24, 87.

<sup>2</sup> *Zeit Zuckerind., Böhmen*, 34, 567.



# ANIMAL ACIDS.

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By PHILIP B. HAWK, M.S., PH.D.

## Kynurenic Acid.

In addition to occurring in the urine of the dog this aromatic hydroxy-acid has been found by Swain<sup>1</sup> in the urine of the coyote. To isolate the acid from urine proceed as follows: Acidify with hydrochloric acid in the proportion 1:25. From the acid fluid both the uric acid and the kynurenic acid separate in the course of 24-48 hours. Filter off the crystalline deposit of the two acids, dissolve the kynurenic acid in dilute ammonia (uric acid is insoluble) and reprecipitate it with hydrochloric acid. Capaldi<sup>2</sup> has proposed a method of estimating kynurenic acid quantitatively.

## Homogentisic Acid.

Alkaptonurics do not possess the power to rupture the benzene nucleus of tyrosine and phenylalanine but eliminate this nucleus in the urine in the form of homogentisic acid. Normal persons disintegrate the nucleus and excrete it as carbon dioxide and water. Abderhalden was able to produce experimental *alkaptonuria* by feeding a normal man with 50 grm. of tyrosine. Garrod classes alkaptonuria, cystinuria, albinism and pentosuria as *inborn errors of metabolism*. The properties and reactions of homogentisic acid are discussed by Mörner.<sup>3</sup>

## Hippuric Acid.

Lewis<sup>4</sup> has demonstrated that the ingestion of 6-10 grm. of sodium benzoate by a normal man is followed by the excretion in the urine of 85-90% of this benzoate in the form of hippuric acid.

Two very satisfactory methods (one volumetric and one gravimetric) for the quantitative estimation of hippuric acid have been proposed by Dakin (see "*Practical Physiological Chemistry*" (Hawk), 5th Ed. p. 520). One of the best of the more recent methods is that suggested by Folin and Flanders.<sup>5</sup>

The procedure with urine is as follows: To 100 c.c. of urine in a porce-

<sup>1</sup> *Am. J. Physiol.*, 1905, 13, 30.

<sup>2</sup> *Zeit. physiol. Chem.*, 23, 92.

<sup>3</sup> *Uppsala Lakare Föreningens Förhandlingar*, 17, 499.

<sup>4</sup> *J. Biol. Chem.*, 1914, 18, 225.

<sup>5</sup> *J. Biol. Chem.*, 1912, 11, 257.



lain evaporating dish add 10 c.c. of 5% sodium hydroxide and evaporate to dryness on a steam-bath (over night). Transfer the residue to a 500 c.c. Kjeldahl flask by means of 25 c.c. of water and 25 c.c. of concentrated nitric acid. Add 0.2 gm. of copper nitrate, a couple of pebbles or glass beads and boil very gently  $4\frac{1}{2}$  hours over a micro-burner. The flasks should be fitted with loosely fitting Hopkin's condensers, through which a good current of water should be flowing to prevent loss of benzoic acid or change in concentration of the nitric acid. After cooling, the condensers are rinsed down with 25 c.c. of water and the contents of the flask transferred to a 500 c.c. separating funnel by the use of 25 c.c. of water. The total volume of the solution should now be 100 c.c. Just enough ammonium sulphate is added to saturate the solution (about 55 gm.), which is extracted four times with washed chloroform using 50, 35, 25 and 25 c.c. portions. The successive portions of chloroform are collected in another separating funnel and treated with 100 c.c. of a saturated solution of sodium chloride to each litre of which has been added 0.5 c.c. of concentrated hydrochloric acid. The mixture is shaken well and the chloroform run into a dry 500 c.c. flask and titrated with *N/10* sodium ethoxide in alcohol using 4–5 drops of phenolphthalein as indicator. The first distinct end-point should be taken. The sodium ethoxide is prepared by dissolving 2.3 gm. of cleaned sodium in 1,000 c.c. of absolute alcohol and may be standardised against pure benzoic acid in washed chloroform.

Haas<sup>1</sup> has devised the following test for the detection of hippuric acid: The material under examination (powder) in the presence of red phosphorus is covered with chloroform; bromine is then added in slight excess and the mixture warmed until a red solution results. A few c.c. of water are added, the bromine and chloroform expelled, the solution cooled, a little protein solution added and sulphuric acid poured down the side of the vessel. A purple zone then develops above the sulphuric acid layer.

### Uric Acid.

The ingestion of 2-phenylquinoline-4-carboxylic acid (atophan) was shown by Nicolaier and Dohrn<sup>2</sup> to cause an increase in the output of uric acid. This finding has been verified by various workers (Weintraud; Frank and Bauch; Deutsch; Zuelzer; Retzlaff; Brugsch; Smith and Hawk and others). In normal cases and in non-gouty cases the uric-acid elimination, under the influence of atophan, is rather large the first day, and falls after a day or two to a point below normal. This is apparently due to the depletion of the supply of uric acid in the blood, and as no urates are deposited, there is no replenishment of the depleted blood. In the case of gout, however, there are deposits, which may be mobilised, tending to maintain the blood

<sup>1</sup> *Trans.*, 1912, 101, 1254.

<sup>2</sup> *Deut. Arch. f. inn. Med.*, 1908, 93, 331.

concentration, thus accounting for the rather high and long-continued increased excretion of uric acid noted in gout cases. Daniels<sup>1</sup> has shown an apparent increase in the uric acid output in gout, over that due to atophan, by the use of lithium. Abl<sup>2</sup> claims that calcium salts, barium sulphate and bismuth nitrate decrease uric acid excretion, whereas santonin, mustard, chloral hydrate, arsenic, strontium, etc., increase the output. This author also claims that the increase in uric-acid output secured by atophan ingestion is augmented by use of calcium salts, barium sulphate, uzara and atropine.

Interesting experiments on the specific rôle of foods in relation to the composition of the urine have recently been reported by Blatherwick.<sup>3</sup> Oranges, raisins, apples, bananas, cantaloups and potatoes, particularly the last two, are very effective in reducing the formation and excretion of acid. Tomatoes are less valuable. The cereals increase the formation of acids. Plums, prunes, and cranberries, in spite of their alkaline ash, increase the excretion of acid, owing to the benzoic acid which they contain. Meat produces a large increase in the acidity of the urine. An increase in the  $H^+$  concentration is accompanied by an increase in titratable acidity and ammonia excretion. All acid urines are supersaturated with uric acid; all alkaline urines may dissolve more uric acid.

**Estimation in Urine: Method of Folin and Denis.**—From 1 to 2 c.c. of urine are measured into an ordinary centrifuge tube by means of a modified Ostwald pipette. A sufficient amount of distilled water is then added to bring the volume of liquid in the tube to about 5 c.c., 6 drops of 3% silver lactate solution, 2 drops of magnesia mixture, and a sufficient amount (10–20 drops) of concentrated ammonia to dissolve the silver chloride, are then added. The tube is now centrifuged for 1 or 2 minutes, the supernatant liquid poured off and to the residue in the bottom of the tube are added 1 drop<sup>4</sup> of concentrated hydrochloric acid and 5 or 6 drops of freshly prepared saturated hydrogen sulphide water, and the tube is placed in a beaker of boiling water until all excess of hydrogen sulphide has been driven off (usually about 5 minutes).

As hydrogen sulphide gives a blue colour with the “uric acid reagent,” care must be taken to obtain its complete removal. To determine whether this has been accomplished, 1 drop of 0.5% lead acetate solution should be added to the contents of the tube after the latter has remained in the water-bath for about 5 minutes, and if any hydrogen sulphide remains a dark-brown precipitate will be formed. If this be the case the tube should be returned to the water-bath for further heating.

When all the excess of hydrogen sulphide has been driven off, the material is centrifuged for 1 or 2 minutes. The supernatant liquid is transferred by decantation to a small beaker, the residue washed in the tube (carefully so as

<sup>1</sup> *Arch. Int. Med.*, 1914, 13, 480.

<sup>2</sup> *Arch. exp. Path. Pharm.*, 1914, 74, 119.

<sup>3</sup> *Arch. Int. Med.*, 1914, 14, 409.

<sup>4</sup> Fine suggests that the single drop of hydrochloric acid is insufficient to make the solution acid and accordingly uses 2 or 3 drops.

to disturb the residue as little as possible) with two portions of 2 c.c. each of distilled water,<sup>1</sup> adding the washings to the material in the beaker.

To the solution containing the uric acid, 2 c.c. of the uric-acid reagent are added and 10 c.c. of saturated sodium carbonate solution, and the mixture is transferred to a 50 c.c. volumetric flask and made up to volume. The colour is then compared with that obtained from 5 c.c. of the standardised uric acid-formaldehyde solution which is treated with 2 c.c. of the uric-acid reagent and 10 c.c. of saturated sodium carbonate solution and diluted to 50 c.c.

In the case of urines containing much protein it will be found that after the addition of hydrogen sulphide the solution obtained is invariably of a brownish tint, which interferes with the colour comparison, and thus makes accurate readings very difficult. This difficulty can be overcome by adding to the hot solution (after removal of all hydrogen sulphide) from 2 to 10 drops of a 10% solution of sodium acetate. Unless albumin be present, sodium acetate should not be added as its presence tends to give slightly low results.

This procedure has also been found useful in estimating uric acid in blood where the same trouble is met with when, as occasionally happens, the protein has not been entirely removed.

**Estimation in Blood: Method of Folin and Denis.**—From 15 to 25 gm. of normal blood are needed for a determination. This is first treated to remove the protein, then concentrated, and the small volume, containing the uric acid, is treated as in the estimation in urine.

The blood is drawn into small, wide-mouthed bottles previously weighed and containing a small amount (about 0.1 gm.) of finely powdered potassium oxalate. From the subsequent weight of each bottle is obtained the weight of the blood. Five times this weight of  $N/100$  acetic acid solution<sup>2</sup> is placed in an ordinary 1000 c.c. flask<sup>4</sup> and heated to boiling. The oxalated blood is then poured into this boiling acetic acid solution, stirring constantly, and the heating is continued until the solution has again begun to boil. The mixture is filtered while still hot. The coagulated material on the filter paper<sup>3</sup> is transferred back into the flask (by means of a small spoon or a spatula), about 200 c.c. of boiling water<sup>4</sup> are poured over it and it is allowed to stand for a few minutes. This mixture is then filtered through the same filter as was used for the first filtration. The filtrate in the receiving flask should be very nearly as clear as water, and will be found to be so if the original blood was promptly shaken with the oxalate so that no clotting has taken place.

If clotting has occurred, the coagulation and washing of the blood is a little more complicated. The clot leads to so much bumping in the boiling

<sup>1</sup> The washing of the precipitate of silver sulphide without disturbing it, is rather unsuccessful, so the tube may be centrifuged for a minute or two after each washing (Smith).

<sup>2</sup> Fine suggests that the pouring of blood into boiling  $N/100$  acetic acid is quite apt to give coloured filtrates, and advises the use of about the same amount of boiling distilled water (i.e., 4 times the weight of blood), bringing this mixture to boiling and then adding enough  $N/100$  acetic acid to bring about complete coagulation. About an equal amount is required.

<sup>3</sup> It was found that the transferring of coagulum could be avoided by using large (400 c.c.) casseroles, for the coagulation, and keeping the coagulum in the casserole rather than allowing it to go on to the filter (Smith).

<sup>4</sup> For this washing, water is used rather than  $N/100$  acetic acid, because if the latter is used the coagulum will give off more or less of the blood pigment and the filtrates will be less clear.

acetic acid solution that it is not practical or safe to try to heat the mixture to boiling. The filtration is, therefore, made earlier. The partially coagulated clot is then broken up with a glass rod, transferred to a mortar, and there ground into a paste in the presence of hot water. This suspension is then poured upon the filter. The protein material on the filter is then washed, as before, with about 200 c.c. of hot water. In this case the combined filtrates are, however, never colourless but more or less reddish. On being heated to boiling a second small coagulum will be obtained and the filtrate will then be practically as clear as water.

The combined filtrate and washings, containing the uric acid and other soluble materials, are further acidified by the addition of 5 c.c. of 50% acetic acid, and are evaporated, over a free flame in a suitable dish,<sup>1</sup> to a very small volume (about 3 c.c.). The liquid is then poured into an ordinary centrifuge tube and the dish washed with two successive portions of 0.1% lithium carbonate solution, using about 2 c.c. for each rinsing. Any solid material adhering to the sides of the dish is removed by rubbing with a rubber tipped stirring rod and added to the solution in the centrifuge tube. This solid material can then be removed from the suspension in the tube by centrifuging—and pouring the supernatant liquid into another tube, washing the sediment with lithium carbonate solution (Smith).

The liquid in the centrifuge tube, which at this stage should not be more than 10 c.c. in volume, is then treated as in the method given for urine.

**Preparation of the Uric Acid Standard.**—The uric acid-formaldehyde solution is prepared as follows: 1 gram. of uric acid is placed in a 1,000 c.c. flask and dissolved by means of an excess of lithium carbonate (200 c.c. of a 0.4% solution). To the solution are added 40 c.c. of 40% formaldehyde solution, and the mixture is shaken and allowed to stand for a few minutes. The clear solution is acidified by adding 20 c.c. of *N*-acetic acid and the whole is diluted to the litre mark with water. The solution should remain perfectly clear and the next day (but not before) it can be standardised against a freshly prepared lithium carbonate solution of uric acid. The colour produced by 5 c.c. of the solution corresponds very nearly with the colour obtained from 1 mg. of uric acid. The colourimeter reading obtained for this solution, when thus compared against 1 mg. of pure uric acid is, of course, thereafter to be used as the standard value corresponding with 1 mg. of uric acid.

**Preparation of the Uric Acid Reagent.**—Add to 750 c.c. of distilled water in a 1,000 c.c. flask, 100 gram. of sodium tungstate, and 80 c.c. of phosphoric acid (85%); boil gently, under a reflux condenser, for about 2 hours. Dilute to a litre.

**References.**—Otto Folin and W. Denis, On the colourimetric determination of uric acid in urine, *J. Biol. Chem.*, 1913, 14, 95.

<sup>1</sup> Deep (half globular) dishes 10 cm. in diameter and having a capacity of 250 c.c. are very good for this purpose. While free flames are the most convenient for concentrating the uric acid solutions care must, of course, be taken not to char the contents towards the end of the operation. Unless the solution can be watched carefully at this stage, it is safer to finish the concentration on the water-bath.

Otto Folin and W. Denis, Determination of uric acid in blood, *J. Biol. Chem.*, 1913, 13, 469.

Private communication from Morris S. Fine.

Smith and Hawk, unpublished data.

### Benzoic Acid.

Benzoic acid is found in the urine of the rabbit and dog. In certain kidney diseases it may also occur in human urine.<sup>1</sup> The benzoic acid apparently arises from the fermentative decomposition of hippuric acid. The ingestion of benzoic acid or benzoates leads to an increased elimination of hippuric acid in the urine. This is due to the fact that within the body synthesis of hippuric acid occurs owing to a conjugation of glycocoll with the benzoic acid or benzoate ingested. This synthesis is believed to be brought about principally by the kidney cells but may also occur elsewhere.<sup>2</sup>

### Oxalic Acid.

Oxalic acid occurs in the urine in the form of calcium oxalate. When the oxalate content of the urine is increased from any cause the condition is called *oxaluria*. This calcium oxalate crystallizes in the form of dumb-bell or octahedral ("envelope") crystals. The origin of the calcium oxalate of the urine is not definitely known. It is eliminated at least in part, unchanged when ingested. Therefore, since many food substances (tomatoes, grapes, asparagus, lettuce, etc.) contain calcium oxalate, it seems likely that a portion of the urinary oxalate originates from the ingested food. Another portion of oxalic acid may be formed in the body in the course of the metabolism of fat and protein. Incomplete oxidation of carbohydrate material may also yield oxalic acid. To prepare calcium oxalate from the urine proceed according to one of the following methods:

**First Method.**—Place 200–250 c.c. of urine in a beaker, add 5 c.c. of a saturated solution of calcium chloride, make the urine slightly acid with acetic acid, and stand the beaker aside in a cool place for 24 hours. Examine the sediment under the microscope and compare the crystalline forms with those shown in Vol. VII, Fig. 26, p. 384.

**Second Method.**—Proceed as above, replacing the acetic acid by an excess of ammonium hydroxide and filtering off the precipitate of phosphates.

### Chondroitin-sulphuric Acid.

This acid is found principally in cartilage from various sources. It may also be formed by the decomposition of chondromucoid, another cartilage constituent. Upon hydrolysing chondroitin-sulphuric acid by means of acid, a nitrogenous substance known as chondroitin is formed, and sulphuric

<sup>1</sup> Jaarsveld and Stokvis, *Arch. exp. Path. Pharm.*, 10.

<sup>2</sup> Kingsbury and Bell: *J. Biol. Chem.*, 1915, 21, 297.

acid results as a by-product. From chondroitin one may then obtain chondrosin, with acetic acid as a by-product. This chondrosin is a reducing substance. Schmiedeberg<sup>1</sup> has shown the formula for chondroitin-sulphuric acid to be  $C_{18}H_{27}O_{17}NS$ . The acid may be obtained in the form of an amorphous white powder which is very soluble in water. For methods of preparation see Schmiedeberg (*loc. cit.*) and Kondo.<sup>2</sup>

### Colloidal Nitrogen.

The so-called "colloidal nitrogen" of the urine consists in large part of oxyproteic, alloxypoteic and autoxyproteic acids. This "colloidal nitrogen" may be precipitated by alcohol or basic lead acetate. It has been claimed that the urine of cancer patients contains abnormally large quantities of "colloidal nitrogen." This claim has not been absolutely substantiated. Some investigators<sup>3</sup> claim that the "colloidal nitrogen" precipitate contains uric acid, purine bases, etc., and is of no diagnostic significance.

### Glycuronic Acid.

Biberfeld<sup>4</sup> claims that glycuronic acid cannot be an intermediary product in the metabolism of glucose, since in his experiments this acid was not utilised by the animal body, but when introduced intravenously was almost completely eliminated in the urine unchanged, or rather in conjugated form.

### Amino-acids.

Recent experiments have made necessary a revision of our ideas regarding the nutritional relationship of these acids. According to the older views, the amino-acids which were formed as end-products of protein digestion in the intestine, were resynthesised in their passage through the walls of the intestine, and appeared in the circulating blood as blood proteins. Careful analysis of the blood failed to show the presence of any amino-acids. Recently, experiments by Folin and Denis, Buglia, Van Slyke and Meyer, and others, have yielded important evidence against the intestinal synthesis of amino-acids. We now know that amino-acids are present in the blood, and the only reason we were unable to detect them heretofore was because of the crudeness of the methods used. The method of Van Slyke, given in Vol. VII, p. 263, is particularly satisfactory for the estimation of amino-acids. The formaldehyde titration method of Sørensen and its modification by Henriques, are also of importance. The first workers who were successful in isolating amino-acids from the circulating blood were Abel and his associates, of Johns Hopkins University. They accomplished this by means of

<sup>1</sup> *Arch. exp. Path. Pharm.*, 28.

<sup>2</sup> *Biochem. Zeit.*, 26.

<sup>3</sup> de Bloeme, Swart and Terwen; *Biochem. Zeit.*, 1914, 65, 345.

<sup>4</sup> *Biochem. Zeit.*, 1914, 65, 479.



their so-called "artificial kidney," or vividiffusion apparatus. By means of this unique apparatus, the blood of a *living* animal may be subjected to dialysis for a period of several hours, and amino-acids, as well as other crystalloids, removed.

### Acetone.

The quantitative estimation of acetone in the blood has recently assumed considerable importance, particularly in case of a pronounced acidosis, such as is frequently met with in diabetes mellitus. The blood of a normal person contains, at most, but a trace of acetone, although this amount may be greatly increased in certain pathological states. Marriott<sup>1</sup> found the blood of normal children to contain 0.06–0.08 mgm. of total acetone (acetone plus diacetic acid) per 100 c.c. In the case of a child in *coma*, the acetone value rose to 23.4. In the author's laboratory, Dr. Bergeim has demonstrated an acetone value of 48.65 mgm. per 100 c.c. of blood serum for the blood of an adult male diabetic in coma.

There are several methods in use for quantitatively estimating acetone in urine. These methods include those of Messinger, Messinger-Huppert, Scott-Wilson, and Folin. The method of the latter, as modified by Hart, for the estimation of total acetone (acetone plus diacetic acid) is as satisfactory as any. The method includes the transformation of the diacetic acid into acetone and carbon dioxide by means of heat; and the subsequent removal of the acetone thus formed, as well as the preformed acetone, by means of an air current as first suggested by Folin. The procedure is as follows: Introduce into a wide-mouthed bottle 200 c.c. of water, an accurately measured excess of *N*/10 iodine solution, and an excess of 40% potassium hydroxide. Prepare an aeration cylinder, containing alkaline hypiodite solution, to absorb any acetone which may be present in the air of the laboratory, and suspend between this cylinder and the bottle (above referred to) a test-tube about 2 in. in diameter. This large test-tube should contain 20 c.c. of the urine under examination, 10 drops of a 10% solution of phosphoric acid, 10 gm. of sodium chloride, and a little petroleum, and should be raised sufficiently high to facilitate the easy application of heat to its bottom portion. The connections on the side of the tube should be provided with bulb-tubes containing cotton. When the apparatus is arranged as described, it should be connected with a Chapman pump and an air current passed through for 25 minutes. During this period the contents of the test-tube are heated just to the boiling-point, and after an interval of 5 minutes again heated in the same manner. By this means the diacetic acid is converted into acetone, and at the end of the 25-minute period this acetone, as well as the preformed acetone, will have been removed from the urine to the absorption bottle, and there retained as iodoform. The contents of the absorption bottle should now be acidified with concentrated

<sup>1</sup> *J. Biol. Chem.*, 1913, 16, 293.

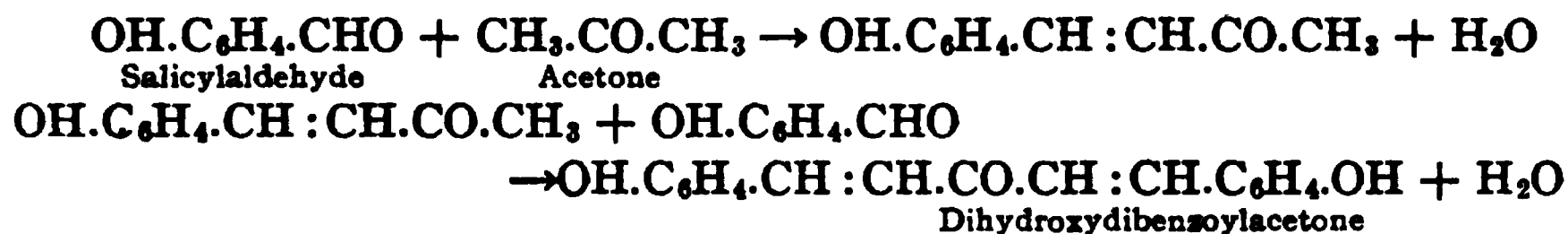


hydrochloric acid and titrated with *N*/10 sodium thiosulphate and starch. (For details and other methods, see "*Practical Physiological Chemistry*" (Hawk), 5th Ed., pp. 533-541).

The nephelometer may be used in estimating minute quantities of acetone as Marriott<sup>1</sup> has shown. Sobel<sup>2</sup> has suggested a quantitative process based on Lieben's test. The iodoform is changed into silver iodide by means of fuming nitric acid and silver nitrate.

Rosenbloom<sup>3</sup> claims that the presence of protein in urine renders inaccurate the detection of acetone by means of Lieben's test. The protein interferes with the production of iodoform, as well as with the deposition of iodoform crystals. It is necessary to distil the urine, and use the distillate in testing.

The test of Frommer<sup>4</sup> is a very satisfactory one. It is based on the fact that acetone reacts with salicylaldehyde to form dihydroxydibenzoylacetone. The chemistry of the test is explained in the following equations:



The chemistry of Legal's colour test, which depends upon the interaction of nitroprusside and acetone, has been studied by Cambi.<sup>5</sup> He claims that the colour reaction is due either to: (I) the formation of a complex ion of ferropentacyanide with the isonitroso compound of the ketone, or to (II) the formation of such an ion with the isonitroamine derivative of the ketone.

### Aceto-acetic Acid.

The quantitative estimation of this acid, in urine and blood, is of considerable importance in connection with acidoses, such as may occur in diabetes mellitus and certain other disorders. The acid may be determined by the process embraced in the Folin-Hart method. The method is as follows: Arrange the apparatus as described under the Folin-Hart method for estimating acetone (see page 576). Start the air current in the usual way, and permit it to run *25 minutes, without the application of heat to the urine under examination*. Under these conditions, the preformed acetone present in the solution is all removed. Immediately attach a freshly prepared absorption bottle containing alkaline hypoiodite solution. Apply heat to the large test-tube as already described *in order to convert the diacetic acid into acetone*, permit the air current to continue for the usual 25 minutes, and determine the diacetic acid value, in terms of acetone, by the usual

<sup>1</sup> *J. Biol. Chem.*, 1913, 16, 289.

<sup>2</sup> *Apoth. Ztg.*, 1914, 52, 62.

<sup>3</sup> *J. Am. Med. Assn.*, 59, 445.

<sup>4</sup> *Berl. Klin. Woch.*, 42, 1008.

<sup>5</sup> *Atti. accad. Lincei*, 1913, 22, I, 376.

titration process. (For details and other methods, see "*Practical Physiological Chemistry*" (Hawk), 5th Ed., page 539.)

### $\beta$ -Hydroxybutyric Acid.

A process of isolating and purifying  $\beta$ -hydroxybutyric acid, in the form of calcium-zinc hydroxybutyrate (a new double salt of calcium and zinc) has been reported by Shaffer and Marriott.<sup>1</sup> The oxidation method for the quantitative estimation of  $\beta$ -hydroxybutyric acid, suggested by Shaffer and given on page 407 of Vol. VII, is a very satisfactory one. The method has been used with success by Gorslin and Cooke,<sup>2</sup> Mondschein,<sup>3</sup> and others. In a re-examination of the method, called forth by the criticism of Embden and Schmitz,<sup>4</sup> Shaffer and Marriott have shown that the process yields 90% of the theoretical values. The results obtained by the method must therefore be corrected by adding one-ninth of the amount found. For use in blood analysis, a slight modification of the above method has been suggested by Marriott.<sup>5</sup>

The *extraction* method suggested by Black<sup>6</sup> is also very satisfactory for the quantitative determination of  $\beta$ -hydroxybutyric acid. The process is as follows: Take 50 c.c. of the urine under examination and make faintly alkaline with sodium carbonate; evaporate to one-third the original volume. Further concentrate to about 10 c.c. on a water-bath, cool the residue, acidify it with a few drops of concentrated hydrochloric acid, and add plaster of Paris to form a thick paste. Permit the mixture to stand until it begins to "set," then break it up with a stout glass rod having a blunt end, and reduce the material to the consistency of a fairly dry coarse meal. Transfer the meal to a Soxhlet apparatus, and extract with ether for 2 hours. At the end of this period evaporate the ether-extract, either spontaneously or in an air current. Dissolve the residue in water, add a little bone-black if necessary, filter until a clear solution is obtained, and make up the filtrate to a known volume (25 c.c. or less) with water. The amount of  $\beta$ -hydroxybutyric acid should then be determined by means of the polarimeter.

Black has also proposed a test, for the detection of  $\beta$ -hydroxybutyric acid, which is very satisfactory. (For details of this test consult Black's original article (*loc. cit.*), or "*Practical Physiological Chemistry*" (Hawk), 5th Ed., p. 441.)

### Bile Acids.

A very satisfactory and simple test to detect bile acids is that of Hay, which is based upon the principle that bile acids have the property of reducing the surface tension of fluids in which they are contained. The test is as

<sup>1</sup> *J. Biol. Chem.*, 1913, 16, 265.

<sup>2</sup> *J. Biol. Chem.*, 1912, 10, 291.

<sup>3</sup> *Biochem. Zeit.*, 1912, 42, 95.

<sup>4</sup> *Handb. d. biochem. Arbeitsmeth.*, 3, 934.

<sup>5</sup> *J. Biol. Chem.*, 1913, 16, 293.

<sup>6</sup> *J. Biol. Chem.*, 5, 207.

follows: Cool about 10 c.c. of urine in a test-tube to 17° C. or lower, and sprinkle a little finely pulverised sulphur upon the surface of the fluid. The presence of bile acids is indicated if the sulphur sinks to the bottom of the liquid; the rapidity with which the sulphur sinks depending upon the amount of bile acids present in the urine. The test is said to show the presence of bile acids when the latter are present in the ratio of 1:120,000. It is claimed by some that this test does not differentiate between bile acids and bile pigments. The modification of the Pettenkofer test (see Vol. VII, p. 420), as proposed by v. Udransky, is also very satisfactory. This modification is as follows: To 5 c.c. of urine in a test-tube, add 3-4 drops of a very dilute (1:1,000) aqueous solution of furfural. Place the thumb over the top of the tube, and shake until a thick foam is formed. By means of a small pipette, add 2-3 drops of concentrated sulphuric acid to the foam, and observe the *dark pink* colouration produced.

A method for the preparation of the unconjugated acid of ox bile has been proposed by Schryver.<sup>1</sup>

The most recent analyses of bile are those reported by Menzies,<sup>2</sup> and Rosenbloom.<sup>3</sup> In each case the bile was obtained from a fistula and the composition (parts per 1,000 by weight) was as follows:

Constituent	Observer	
	Menzies	Rosenbloom
Bile salts.....	4.2	10.1
Mucin and pigments.....	9.3	4.86
Cholesterol.....	0.94	2.61 <sup>4</sup>
Fat.....	2.98 <sup>4</sup>	6.85
Soaps.....		2.6
Lecithin.....	not determined	6.42
Total solids.....	22.5	29.8
Inorganic.....	5.8	9.2
Water.....	974.5	970.2
Fatty acids.....	not determined	1.2

### Bile Pigments.

The following process to estimate the bile pigments has been suggested by Czynlary, Fuchs and v. Furth:<sup>6</sup> 5 c.c. of bile are heated with 5 c.c. of 10% sodium hydroxide for 30 minutes on a steam-bath under a reflux; this treatment changing the bilirubin to biliverdin. The solution is mixed with 30 c.c. of 95% alcohol and the precipitate formed is removed by filtering. The filtrate is cleared by adding a few drops of hydrochloric acid and the green solution is compared in a colourimeter with a 0.02% alcoholic solution of Schuchardt's biliverdin.

<sup>1</sup> *J. Physiol.*, 44, 275.

<sup>2</sup> *Biochem. J.*, 1912, 6, 210.

<sup>3</sup> *J. Biol. Chem.*, 1913, 14, 241.

<sup>4</sup> Includes lecithin and fatty acids.

<sup>5</sup> Contained a trace of cholesterol esters.

<sup>6</sup> *Biochem. Zeit.*, 49, 120.

Apart from the tests for bile pigments mentioned in Vol. VII, p. 425, the following tests are often employed:

**Salkowski-Schipper's Test.**—Neutralise the acidity of 10 c.c. of the urine under examination with a few drops of a dilute solution of sodium carbonate, and add 5 drops of a 20% solution of sodium carbonate and 10 drops of a 20% solution of calcium chloride. Filter off the resultant precipitate, upon a hardened filter paper, and wash it with water. Remove the precipitate to a small porcelain dish, add 3 c.c. of an acid-alcohol mixture (made by adding 5 c.c. of concentrated hydrochloric acid to 95 c.c. of 96% alcohol) and a few drops of a dilute solution of sodium nitrate, and heat. The production of a green colour indicates the presence of bile pigments.

**Bonanno's Test.**—Place 5–10 c.c. of the urine under examination in a small porcelain evaporating dish and add a few drops of Bonanno's reagent (2 gm. of sodium nitrite in 100 c.c. of concentrated hydrochloric acid). If bile is present an emerald-green colour will develop. Bonanno says the test is not interfered with by any known normal or pathological urinary constituent.

### Urinary Calculi.

Among the more recent analyses of urinary calculi are those of Kahn and Rosenbloom.<sup>1</sup> They analysed 24 calculi and showed 18 of them to contain over 60% of calcium oxalate; the 6 which contained less than 60% of calcium oxalate gave an average of 56%  $P_2O_5$ . All contained uric acid or urates, but only 3 of the 24 contained more than 10%. The authors claim that the shape, colour and consistency of a stone do not form a criterion of its composition. Two cystic calculi contained no calcium oxalate but 96.3% and 98.0% of uric acid respectively. The authors suggest acid treatment for oxalate calculi and alkali treatment for uric acid calculi.

A graphic scheme for use in the examination of urinary calculi, radically different from that given in Vol. VII, may be found in "*Practical Physiological Chemistry*" (Hawk), 5th Ed., p. 477.

### Hydrochloric Acid.

Hydrochloric acid is manufactured in the human stomach by cells in the gastric mucosa. There are several theories as to the origin of this hydrochloric acid, *e.g.*, the *mass action* theory of Bunge, the *electrolytic dissociation* theory of Köppe, and the *phosphonuclease* theory of Bergeim.<sup>2</sup> The normal acidity of the human gastric juice has been placed at 0.2% HCl. However, recent investigations<sup>3</sup> have shown that the acidity of the gastric juice as secreted is probably about 0.4–0.5% HCl. Boldyreff (*loc. cit.*) claims that

<sup>1</sup> *J. Am. Med. Assn.*, 1913, 59, 2252.

<sup>2</sup> *Proc. Soc. Exp. Biol. Med.*, 1914, 12, 21.

<sup>3</sup> Babkin, "*Die äussere Sekretion der Verdauungsdrüsen*," Berlin, 1914; Boldyreff, *Quart. Jour. Expt. Physiol.*, 1914, 8, 1; Bergeim, Rehfuß and Hawk, *J. Biol. Chem.*, 1914, 19, 345; and others.

this acidity may be reduced to 0.2% by the regurgitation of alkaline juices from the intestine.

When the acidity of the gastric juice is increased to any extent above normal, a condition known as *hyperacidity* results; a decrease from normal is called *hypoacidity*. The volume of the gastric juice as well as its acid concentration may be increased by water ingestion.<sup>1</sup> Milk, and the extractives of meat, are also active gastric stimulants. A psychical stimulation may be brought about through the thought or sight of food. The hydrochloric acid of the gastric juice forms a medium in which the pepsin can most satisfactorily digest protein food. The acid acts also as a germicide, thus preventing putrefaction from taking place in the stomach, and possesses the power of inverting cane sugar. When protein food reaches the stomach it combines with the hydrochloric acid and forms so-called "combined hydrochloric acid," which is really a *protein salt* of hydrogen chloride and behaves differently from the *free* acid. In gastric analysis, the acid concentration may be determined by estimating the  $H^+$  concentration, or by titrating with phenolphthalein as indicator for *total* acidity, and with Sahli's reagent (see Sahli's "*Diagnostic Methods*") for *free* acidity.

<sup>1</sup> Wills and Hawk, *J. Am. Chem. Soc.*, 1914, 36, 158; Foster and Lambert, *J. Exptl. Med.*, 1908, 10, 820; Bergeim, Rehfuess and Hawk, *J. Biol. Chem.*, 1914, 19, 345.

# LACTIC ACID.

By W. A. DAVIS.

**Qualitative Tests.**—According to Neuberg<sup>1</sup> the statement frequently found in text-books that sarcolactic acid (*d*-lactic acid) does not give the iodoform reaction (compare Vol. VII, p. 435) is not correct as both *d*- and *l*-lactic acids respond to this test. Pyruvic acid, aldol,  $\beta$ -hydroxybutyric acid, quercitol and inositol also give a positive result under the same conditions, but in these cases the yellow precipitate formed, which has the characteristic odour of iodoform, may perhaps be a homologue of the latter.

**British Pharmacopœia, 1914.**—In the new pharmacopœia lactic acid (*Acidum Lacticum*) is defined as “an aqueous solution containing not less than 75% by weight of hydrogen lactate,  $\text{HC}_2\text{H}_3\text{O}_3$ , and not less than 100% by weight of lactide,  $\text{C}_6\text{H}_8\text{O}_4$ . Sp. gr. about 1.21.” This definition is not in accord with the view generally held that the substance derived from the lactic acid during concentration is principally lactic anhydride and not lactide. The other requirements are as follows: “1 grm. diluted with 10 c.c. of water requires for neutralisation not less than 8.3 c.c. of *N*/1 solution of sodium hydroxide. After the further addition of 10 c.c. of the alkaline solution and boiling for 15 minutes not more than 8.6 c.c. of *N*/1 solution of sulphuric acid are required to neutralise the excess of alkali. Yields no characteristic reactions for calcium, iron, chlorides, citrates, oxalates, phosphates, sulphates or tartrates. *Lead limit* 10 parts per million. *Arsenic limit* 5 parts per million.” The remaining tests are the same as given in Vol. VII, p. 446.

**Estimation of Lactic Acid in Organic Tissues and Extracts in Presence of  $\beta$ -Hydroxybutyric Acid and Other Substances.**—According to Mondscheim<sup>2</sup> previous determinations of the lactic acid in flesh have been too low owing to the fact that about one-third of the acid is carried down with the coagulated albumin and escapes estimation. The lactic acid in a decoction of muscular fibre can be estimated with sufficient accuracy by direct titration using phenolphthaleïn as indicator, since other acid substances are not present in appreciable quantities under normal conditions. The portion retained by the coagulated albumin may be estimated by boiling the latter with solution of alkali, precipitating the albumin from the solution of albuminate by adding a saturated solution of sodium chloride and estimating the lactic acid in the filtrate by oxidation into acid permanganate solution (see below).

<sup>1</sup> *Biochem. Zeitschr.*, 1912, 43, 500.

<sup>2</sup> *Biochem. Zeitschr.*, 1912, 42, 91 and 105.

When  $\beta$ -hydroxybutyric acid is present as well as lactic acid Mondschein adopts the following process. Separate portions are taken for the analysis. In one of these the lactic acid is oxidised by potassium permanganate in 1% sulphuric acid by the method of Fürth and Charnass (see Vol. VII, p. 439), the products consisting of acetaldehyde from the lactic acid and a certain amount of acetone from the  $\beta$ -hydroxybutyric acid. The distillate is divided into two parts in one of which the absorption value for sulphurous acid is determined by Ripper's method of titration into iodine<sup>1</sup> whilst the second is freed from acetaldehyde, by boiling with alkali and hydrogen peroxide, beneath a reflux condenser, and is then again distilled and titrated according to Ripper's method. The difference between the two results is due to the acetaldehyde present in the first distillate and is calculated as *lactic acid*. The other portion of the original distillate is oxidised with 0.5% potassium dichromate solution in 4% sulphuric acid which oxidises the  $\beta$ -hydroxybutyric acid to acetone and a little of the lactic acid to acetaldehyde. The mixture is distilled, the second distillate freed from acetaldehyde as before and the acetone distilled and estimated volumetrically by means of iodine and thiosulphate; the acetone found is calculated as  $\beta$ -hydroxybutyric acid.

According to Oppenheimer<sup>2</sup> the method used by Mondschein of liberating the lactic acid from proteins by means of boiling 10% sodium hydroxide is open to several objections and he recommends precipitating the proteins with hydrochloric acid and mercuric chloride as proposed by Schenk. In comparative experiments with blood, muscle and yeast-juice it was found possible to recover, by the latter method over 96% of the lactic acid added to these fluids. Colloidal iron used as precipitant is not satisfactory as a loss of about 30% of the lactic acid occurs therewith.

Bellet<sup>3</sup> gives the following details of a method of estimating lactic acid in substances such as blood, urine, etc., based on its conversion into acetaldehyde by permanganate. The liquid is first freed from proteins by means of Patein and Dufau's reagent (an acid solution of mercuric nitrate) and is then neutralised and evaporated to a syrup; the latter is acidified with sulphuric acid, mixed with anhydrous sodium sulphate and sand, and extracted with ether in a Soxhlet apparatus. The ethereal extract is evaporated, the residue dissolved in water, transferred to a flask and diluted to 200 c.c. The flask is connected with a condenser the lower end of which passes into an absorption vessel; this in turn is connected with a second similar vessel and condenser. The absorption vessels contain a definite volume of a solution of silver nitrate (15 grm. silver nitrate, 150 grm. ammonia and 100 c.c. sodium hydroxide solution, the mixture being diluted to 500 c.c.). The liquid in the flask is made strongly acid with sulphuric acid, heated to boiling and a 1.5% solution of potassium permanganate added drop by drop at such a rate that each drop is decolourised before the next is intro-

<sup>1</sup> *Monatsh.*, 1900, 21, 1079.

<sup>2</sup> *Zeit. physiol. Chem.*, 1914, 89, 39.

<sup>3</sup> *Bull. Soc. Chim.*, 1913, 13, 565.



duced; a current of air is kept passing through the apparatus so as to carry over the acetaldehyde as fast as it is formed. When the permanganate is no longer decolourised the solution is boiled for an additional 3 minutes, the contents of the receivers are mixed, filtered and the excess of silver is titrated. The presence of  $\beta$ -hydroxybutyric acid, succinic and oxalic acids does not interfere with the estimation of lactic acid by this method.

It is probable that the methods described above, depending upon the oxidation of lactic acid to acetaldehyde, a change which is difficult to regulate so that it shall take place quantitatively, are not so accurate as the method described in Vol. VII, depending on the separation of the zinc salt (Vol. VII, pp. 437 and 451). Wolf<sup>1</sup> has recently described experiments emphasising this; he shows that the estimation by the aid of the zinc salt in general is far more satisfactory than by oxidation methods. In concentrating the fluids for analysis, they should be evaporated *in vacuo* at as low a temperature as possible so as to avoid loss of the acid. The extraction from the concentrated solution by ether is best accomplished by absorbing the solution on blotting paper and extracting in a Soxhlet apparatus three or four times. Wolf, like Oppenheimer (*supra*), uses Schenk's method to remove the proteins.

For other methods of estimating latic acid see page 608.

**Estimation of Lactic Acid in Urine.**—Baragiola and Schuppli<sup>2</sup> describe a modification of Möslingers method (Vol. VII. p. 438), as the latter is likely to give unreliable results owing to the reduction of barium chloride by carbon, to the retention of lactic acid by the substances insoluble in alcohol and to the conversion of the lactic acid by malic acid into a compound in which the former is not estimated. The modified method is as follows: 25 c.c. of the urine, mixed with 25 c.c. of water, are distilled with steam until 200 c.c. of distillate have been collected; 5 c.c. of 10% barium chloride are added to the distillate and the latter neutralised with saturated barium hydroxide. In case lactic anhydride is present, an excess of barium hydroxide may be added, the solution heated over the water-bath and neutralised with hydrochloric acid using azolitmin as indicator. The neutral solution is evaporated to 15 c.c., transferred to a 100 c.c. cylinder, diluted with water to 25 c.c. and 95% alcohol added drop by drop, shaking well. The mixture is diluted to 100 c.c. with alcohol, filtered after 24 hours, and 75 c.c. of the filtrate mixed with 25 c.c. of 5% solution of sodium sulphate. The barium sulphate is filtered off and 75 c.c. of the filtrate are evaporated to dryness. The residue is incinerated, the ash dissolved in water and the boiling solution titrated with *N*/10 acid.

<sup>1</sup> *J. Physiol.*, 1914, 48, 341.

*Zeitsch. Nahr. Genussm.*, 1914, 27, 841.

# CYANOGEN AND ITS DERIVATIVES.

By HERBERT PHILIPP.

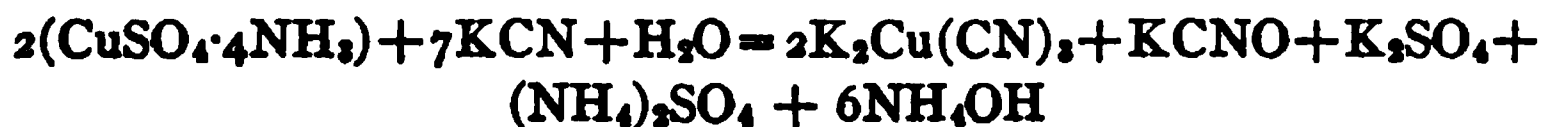
**Spectroscopic Detection of Cyanogen.**—W. Grotrian and C. Rung<sup>1</sup> report on the so-called "cyanogen bands." A Schönherr's arc which was filled with nitrogen, that was also mixed with other products (CO<sub>2</sub>, etc.) between copper, iron, platinum, aluminium and carbon electrodes, proved that the so-called cyanogen bands were due to nitrogen and that cyanogen cannot be detected spectroscopically.

## Hydrocyanic Acid and Simple Cyanides.

**Sodium cyanide**, NaCN, has a solubility of 51.7 grm. in 100 c.c. water and the salt melts at 560°.

**Gold cyanide** compounds have been recommended for therapeutical use in the treatment of tuberculosis and syphilis, generally together with organic bases to prevent the reduction of the gold cyanide. Its therapeutical value is, however, disputed by some authorities.

**Detection of Hydrocyanic Acid and Cyanides.**—O. L. Barnely<sup>2</sup> proposes a new method of detecting cyanides in the presence of ferro- and ferricyanides and thiocyanates which depends on the solubility of cupric sulphide in alkali cyanide solutions. When hydrogen sulphide is passed into a dilute ammoniacal cupric solution a precipitate of cupric sulphide is formed, or a deep blue to brownish-black colouration is imparted to the solution. The addition of an alkali cyanide clears this suspension or coloured solution; ferro- as also ferricyanides and thiocyanates do not disturb the reaction. The test is carried out with quite dilute copper solutions, an ammoniacal solution of 1.25 grm. CuSO<sub>4</sub>·5H<sub>2</sub>O to the litre being used. Each c.c. of this solution is equivalent to about 0.000473 grm. of hydrocyanic acid. The theoretical action is



The approximate amount of alkali cyanide can be estimated by this method.

C. Pertusi and E. Gastaldi<sup>3</sup> describe a method to detect hydrocyanic acid and cyanides. A few drops of a 3% copper acetate solution are put into a test-tube to which is added 1 c.c. of a 10% disodium phosphate solution and 4

<sup>1</sup> *Phys. Zeit.*, 1914, 15, 545.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1914, 36, 1092.

<sup>3</sup> *Chem. Zeit.*, 1913, 37, 609.

drops of a saturated benzidine acetate solution. To this the solution to be tested is added drop by drop. It is necessary to add the solution to the reagents and not *vice versa* as the cyanogen liberated through the copper salt from the cyanide only reacts instantaneously *in statu nascendi*. By using these precautions, a distinct blue violet colouration is obtained by adding 6 drops of a solution containing 0.000027 gm. HCN per c.c.

If the solution to be tested contains a large amount of sulphocyanide action will take place in the absence of cyanides and in this case the method must be carried out as follows: The material to be tested must be, as is generally the case with acids, boiled with a solution of sodium carbonate. The filtered solution is placed in a gas wash-bottle and a current of carbon dioxide, washed by means of a solution of sodium carbonate, is passed through. The carbonic acid being a stronger acid expels the hydrocyanic acid from the alkali cyanide.

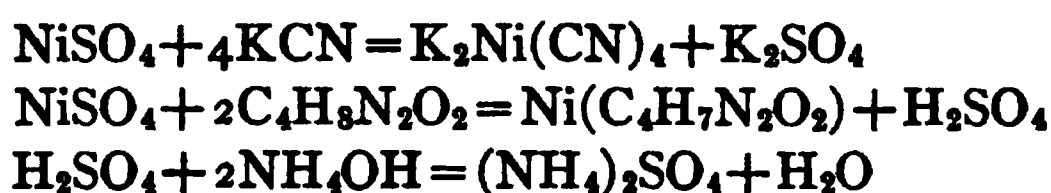
Iron, cobalt, manganese, *i.e.*, such metals which in alkali solution with cyanides form double salts, must not be present.

This last described method is especially delicate. In 10 c.c. of liquid 0.000007 gm. hydrocyanic acid are distinctly traceable, quantities which do not show by the Prussian blue reaction.

This test is also recommended to detect nitrogen in organic compounds after conversion into cyanide by metallic sodium, further for the examination of gas, contaminated air, etc.

**Estimation of Hydrocyanic Acid and Cyanides.**—A method of estimating hydrocyanic acid and the alkali cyanides has been worked out by G. E. F. Lundell and J. A. Bridgman.<sup>1</sup>

This new method is based upon the titration of an ammoniacal hydrocyanic acid solution with nickel ammonium sulphate solution in the presence of dimethylglyoxime. The characteristic red colouration of the nickel dimethylglyoxime appears only after all of the cyanide is bound as the nickel double salt. The changes involved are as follows:



No permanent red precipitate of nickel dimethylglyoxime is formed until all of the cyanide has been used up according to the first equation. The ammoniacal cyanide solution is used since free sulphuric acid hinders the precipitation of nickel dimethylglyoxime.

The reagents required consist of a solution of 15.3 gm. of nickel ammonium sulphate in 1000 c.c. water to which is added 2 c.c. of concentrated sulphuric acid (50 c.c. shall be equivalent to 1 gm. KCN) and a solution of 8.9 gm. of dimethylglyoxime in 1000 c.c. 95% alcohol.

To carry out the estimation 5 gm. of the sample are dissolved in water and

<sup>1</sup> *J. Ind. and Eng. Chem.*, 1914, 6, 554.

diluted to exactly 500 c.c. 50 c.c. of this solution are diluted with an equal volume of water treated with 1 c.c. of ammonium hydroxide and 0.5 c.c. of the dimethylglyoxime solution and then titrated with the nickel solution until a permanent red precipitate is produced. The results agree well with other methods. The presence of double cyanides, except potassium zinc cyanide, does not disturb the method.

A new and excellent method of estimating halogens in alkali cyanides is described by Polstorff and Meyer.<sup>1</sup> Exactly 0.6 grm. of substance is dissolved in 100 c.c. distilled water. If it is necessary to make the solution alkaline, precautions must be taken to ensure that the sodium or potassium hydroxide used is absolutely free from halogens. 20 to 30 drops of commercial formaldehyde solution (35%) are added to the alkaline solution, which is allowed to stand for 15 minutes and then acidified carefully with 30% nitric acid (5 c.c. usually suffices). The halogen is estimated in the solution by the Volhard Method described in Vol. VII, p. 553.

### Double Cyanides.

**Sodium Zinc Cyanide.**—N. Herz<sup>2</sup> reports that sodium zinc cyanide,  $\text{Na}_2\text{Zn}(\text{CN})_{4,3}\text{H}_2\text{O}$ , crystallises from pure solutions of sodium zinc cyanide which are free from less soluble salts and from excessive amounts of free alkali. One part of this hydrated salt is soluble in 0.47 part water at 15°. The crystals are orthorhombic, simple in form, either flat diamonds or pseudo-hexagonal plates. They are brilliant when removed from the solution but effloresce rapidly, becoming dull and chalky. The dry salt is quite stable in air, being completely soluble in water after several days' exposure. Even after complete dehydration at 105° there was very little evidence of decomposition.

### Compounds of Cyanogen and Iron.

On page 503, Vol. VII, line 2,  $\text{Fe}^{\text{III}} \begin{matrix} \diagup (\text{CN})_3 \\ \diagdown (\text{CN})_3 \end{matrix} =$

should read  $\text{Fe}^{\text{III}} \begin{matrix} \diagup (\text{CN})_3 \\ \diagdown (\text{CN})_3 \end{matrix} \equiv .$

In 1912 I. Guareschi discovered that a fuchsine solution decolourised with sulphurous acid was the best reagent for detecting bromine.<sup>3</sup> He later applied this method to detect bromides in the presence of ferro- and ferricyanides.<sup>4</sup> The fuchsine solution is prepared by dissolving 1 grm. fuchsine hydrochloride in 1000 c.c. distilled water, to which is added, whilst stirring, 8 c.c. of a saturated sodium bisulphite solution and about 10 c.c. hydrochloric acid (1.19 sp. gr.). Starch-free filter paper is saturated with this solution for

<sup>1</sup> *Zeit. anal. Chem.*, 1912, 51, 601.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1914, 36, 912.

<sup>3</sup> *Zeit. f. anal. Chem.*, 1913, 52, 538.

<sup>4</sup> *Atti R. Accad. Sci. Torino*, 1913, 49, 15.

use in detecting bromine, which forms a blue colour when it comes into contact with this paper or the solution as prepared above. To carry out the test the material to be tested is usually treated dry or in solution with a 50% solution of chromic acid, gently heated with a piece of the test paper in the neck of the flask, when the presence of bromides can be detected by the blue colouration of the paper.

0.001 grm. potassium bromide can be detected in 1 grm. of potassium ferro- or ferricyanide. Smaller amounts can be detected by treating the powdered material with a 25% chromic acid solution. This method can also be used to detect bromides in Prussian blue.

**Estimation of Ferrocyanides.**—L. L. de Koninck and N. Joastart<sup>1</sup> have suggested the use of alkali bromate for the titration of ferrocyanides instead of that of permanganate solution. The advantage claimed is that no foreign metals enter the solution which might be precipitated by using the solution for further analysis. The titration takes place in acid solution and iron alum is used as indicator.

**Estimation of Hydroferricyanic Acid in the Presence of Ferric and Cyanogen Ions.**—E. Müller and F. Seidel<sup>2</sup> have worked out a satisfactory method of estimating ferricyanides in the presence of ferric salts and cyanides. The method depends on the introduction of potassium fluoride into the solution, which has the effect of preventing the liberation of iodine from potassium iodide in the presence of ferric salts whilst not interfering with its liberation from potassium iodide by ferricyanide salts.

The ferricyanide solution containing a ferric salt is treated with an excess of potassium fluoride solution (0.386 grm. per c.c.) in relation to the quantity of ferric salt present, then with potassium iodide and finally with some zinc sulphate solution. It is necessary to add the zinc sulphate solution last as otherwise zinc ferricyanide is formed which liberates iodine from the potassium iodide very slowly. The liberated iodine is titrated with sodium thio-sulphate as described in Vol. VII, p. 528.

If cyanogen ions are present it is necessary to add a few drops of sulphuric acid and to expel the hydrocyanic acid by a current of carbon dioxide gas, which is first passed through a potassium permanganate solution so as to be sure that it is free from reducing gases. If the hydrogen cyanide is passed through a wash bottle containing silver nitrate solution it can be estimated quantitatively at the same time.

### Carbonyl Ferrocyanides.

H. E. Williams<sup>3</sup> states that compounds of hydrocarbonyl-ferrocyanic acid,  $H_2FeFe(CN)_5CO$ , exist in the mother liquor resulting from the working up of cyanogen mud, better known as spent purifying mass of

<sup>1</sup> *Chem. Zeit.*, 1914, 38, 1084.

<sup>2</sup> *Zeit. anal. Chem.*, 1914, 53, 416.

<sup>3</sup> *Proc. Chem. Soc.*, 1913, 29, 10.

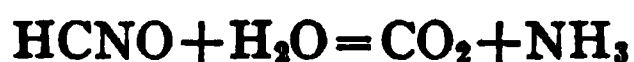
gas works. The carbonyl-ferrocyanic radical is recovered by precipitating with ferric salts, boiling the precipitate with lime and precipitating the ferrocyanide present as calcium ammonium ferrocyanide. The filtrate is boiled with lime and the salt allowed to crystallise. The salts of the alkali and alkali earth metals, including lithium and magnesium, are very soluble and several are deliquescent. The salts of the heavy metals are for the most part insoluble in water. Lead, chromic, stannic, and aluminium salts produce no precipitate.

### Thiocyanates, Sulphocyanides.

Guareschi's test (see page 587) can also be used to detect bromides in the presence of sulphocyanides by treating either the substance or a concentrated solution of the same with chromic acid. More precautions have to be taken in this determination than described under ferrocyanides. The process is carried out as follows: A mixture of 0.5 gm. potassium sulphocyanide and 0.001 gm. potassium bromide are carefully treated with 10 c.c. of a 50% chromic acid solution. When the vigorous action has subsided the mixture is gently heated until it boils, care being taken that the long-necked flask does not become too hot from the steam. If now a gentle stream of air is passed through the flask the decolourised fuchsine test paper (see page 588) becomes blue. This method will detect the presence of 0.0003 gm. potassium bromide in 0.5 gm. potassium sulphocyanide.

In detecting bromides in ammonium sulphocyanide it is best to treat the substance with an excess of 5 or 10% chromic acid solution.

If potassium permanganate is used instead of chromic acid for oxidising, errors are liable to ensue as the formed cyanate salt easily decomposes, producing ammonia according to the following equation:



The liberated ammonia gives a light red colour to the fuchsine reagent which might easily cover the blue produced by the bromine. This method can be used in the presence of iodides and chlorides.

### Cyanamide.

A. P. Lidow<sup>1</sup> states that the commercial cyanamide salts lose their nitrogen by storing in the atmosphere. Calcium cyanamide is claimed to lose up to 32.62%, whilst sodium cyanamide loses up to 33.8% of the original nitrogen. The loss of nitrogen is not only connected with the escape of ammonia, but also due to the formation of  $\alpha$ -oxane salts.

The small quantities of unconverted carbide left in the commercial calcium cyanamide (lime nitrogen) can become dangerous on storing in a

<sup>1</sup> *Chem. Zeit.*, 1914, 38, 574.

closed space, as was the case last January<sup>1</sup> when 600 sacks on board a ship in Trieste harbor evolved enough acetylene to create a violent explosion. This calcium cyanamide was packed in sacks, but it has been ordered in future to pack this material in iron drums for transportation.

On page 558, Vol. VII, a method is described for the estimation of calcium cyanamide which has been modified by G. Grube and J. Krüger<sup>2</sup> who proceed as follows: An alkali or alkali earth cyanamide solution containing 60 grm. cyanamide to the litre is used. 10 c.c. of this solution are made up to 100 c.c. and of this dilute solution 10 c.c. are placed in a 500 c.c. measuring flask which contains 300 c.c. of water acidified with 1 c.c. 2*N* nitric acid. To this solution are added 50 c.c. of *N*/10 silver nitrate solution and so much 2% ammonium hydroxide solution that a piece of litmus paper placed in the solution just turns blue. The flask is then filled to the mark, vigorously shaken until the precipitate gathers together; 250 c.c. of the filtered solution are titrated with *N*/10 ammonium thiocyanate to estimate the excess silver used. It was found that a large excess of ammonium hydroxide or ammonium salts gave erroneous results on account of the solubility of silver cyanamide in such solutions.

<sup>1</sup> *J. Frank. Inst.*, 1914, 178, 247.

<sup>2</sup> *Zeit. angew. Chem.*, 1914, 27, 326.



# ENZYMES.

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By E. FRANKLAND ARMSTRONG.

For the investigation of problems concerning plant oxydases (see Vol. VIII, p. 12) it is probable that the best results will be gained by using several oxydase reagents to find that most suited for the particular case. One of the most satisfactory reagents is benzidine, used either in  $\frac{1}{2}\%$  solution in 50% ethyl alcohol or as a saturated solution in 1 or 2% sodium chloride (compare Keeble and Armstrong).<sup>1</sup> Blue or violet brown colourations or precipitates are obtained when the reaction is positive, owing to the formation of *meri*-quinonoid salts of diphen-quinonediimine with benzidine.

According to Bach,<sup>2</sup> guaiacol is the most suitable substance for testing the sensitiveness of the peroxydase reaction on account of its relative resistance to hydrogen peroxide in the absence of a catalyst. He uses a 0.1% solution of guaiacol in water.

Chodat<sup>3</sup> has shown that a remarkable range of coloured compounds is produced when a vegetable oxydase acts on *p*-cresol in presence of an amino-acid, polypeptide or peptone, according to the nature of the amino-compound.

Bunzel<sup>4</sup> describes a simplified apparatus for measuring the oxydase in liquids, in which the plant juice and a solution of an oxidisable substance are mixed under known conditions and the change in volume due to the oxygen absorbed in the action is measured.

Kober<sup>5</sup> applies the estimation of suspensoids by means of the nephelometer to the study of enzymes. In the case of the nucleases, undigested nucleic acids are precipitated by a 0.2% solution of egg albumin faintly acidified with acetic acid.

<sup>1</sup> *Proc. Roy. Soc.*, 1913, 87B, 125.

<sup>2</sup> *Ber.*, 1914, 47, 2122.

<sup>3</sup> *Arch. Sci. phys. nat.*, 1912, [iv], 33, 70.

<sup>4</sup> *Chem. Soc. Abstracts*, 1913, II, 508.

<sup>5</sup> *J. Amer. Chem. Soc.*, 1914, 36, 1304.

# PROTEINS.

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By S. B. SCHRYVER, PH.D., D. Sc.

**Estimation of Aspartic and Glutamic Acids in the Products of Protein Hydrolysis.**—F. W. Foreman<sup>1</sup> has described the following method: If calcium hydroxide is added to the hydrolysis mixture (after evaporating off the greater part of the hydrochloric acid used *in vacuo*), and then alcohol, the calcium salts of glutamic and aspartic acids are precipitated quantitatively together with other substances. If the free acids are regenerated from the calcium salts, they are obtained in a crystalline form and can be separated from pyrrolidinecarboxylic acid and other substances, which up to the present have not been identified, by treatment with cold glacial acetic acid in which the aspartic and glutamic acids are insoluble. The proportion of the two acids can be determined by estimating the carbon in the mixture or by separating them by means of the copper salts. The pyrrolidinecarboxylic acid can be estimated in the acetic acid extract by determining the amino-nitrogen in weighed portions before and after hydrolysis with hydrochloric acid, an operation which causes its conversion into glutamic acid. It appears that under the conditions employed up to the present, some glutamic acid is converted into pyrrolidinecarboxylic acid during the operations, but it is believed that a modification of the conditions will be found under which this change will be avoided.

<sup>1</sup> *Biochem. J.*, 1914, 8, 463.

# VEGETABLE PROTEINS—FLOUR.

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By E. FRANKLAND ARMSTRONG.

Modern milling practice—in particular the processes of improving and conditioning—has directed attention to the testing of wheat and flour for moisture, phosphate, sulphate, nitrite, etc.

The degree of bolting or dressing of flour is best determined by eye. According to Lindet<sup>1</sup> the cellulose content forms an accurate basis for evaluation.<sup>2</sup>

Frequent estimations of moisture are now a matter of necessity in scientific milling and quick and reliable methods of testing are required. The methods based on heating the grain in a mineral oil in suitable apparatus and measuring the water which distils over take about half an hour. In any method of determining moisture the influence of fluctuations of a few degrees in the temperature to which the grain or flour is heated must not be overlooked. (See in this connection S. Lovatt, *J. Ind. Eng. Chem.*, Jan., 1910.)

The recent extension of the use of processes of conditioning and bleaching in milling brings the search for the presence of improvers in flour within the analyst's range. The commonest of these are acid calcium phosphate with or without acid ammonium phosphate. These are often sold mixed with flour. The presence of calcium sulphate in any considerable proportion is to be regarded as an adulteration. Another type of improver consists of potassium persulphate,  $K_2S_2O_8$ . "Salox" is stated to contain 2% of this salt mixed with flour; only 1 ounce is said to be required for a sack of flour, so that its detection is practically impossible.

Treatment of flour by spraying with soluble improvers—generally soluble phosphates—leads to an increase of phosphate in the flour. This can be detected by analysis only if a typical flour of similar origin is available for comparison. As flours from the same locality vary a good deal from season to season in their content of phosphate, no empirical standard can be given.

It is impossible to determine sulphates in the ash of flours as the acid phosphates present decompose sulphates on ignition. The method proposed by Cripps and Wright<sup>3</sup> is to shake 100 grm. of flour with 1,000 c.c. of 1% acetic acid for 1 hour, then take 500 c.c., boil this with hydrochloric

<sup>1</sup> *Bull. Soc. Chim.*, 1914, 15, 384.

<sup>2</sup> *Chem. Soc. abstracts*, 1914, II, 500.

<sup>3</sup> *Analyst*, 1914, 39, 429.

acid, nearly neutralise, precipitate the proteins with Almen's tannin reagent, filter and estimate the sulphate in the filtrate.

In various flours examined the amount varied from 0.0069 to 0.0084% of  $\text{SO}_3$ .

R. T. Thomson<sup>1</sup> heats about 20 grm. of flour with dilute hydrochloric acid until the starch is liquefied, and determines sulphates in the filtrate by means of barium chloride. He states that first-grade flour contains 0.01 to 0.013% of  $\text{SO}_3$ , whilst third grade contains 0.061%.

According to R. T. Thomson ordinary wheaten flour is neutral to litmus and methyl-red, alkaline to methyl-orange, and acid to phenolphthalein. During milling, nitrite equivalent to about 0.35 part of  $\text{NaNO}_2$  per million may be absorbed from the atmosphere.

According to Thatcher and Koch<sup>2</sup> a quantitative extraction of diastase from flour can be made by shaking with water at  $0^\circ$  from 1 to 2 hours. The liquid is filtered cold and the diastatic power estimated immediately.

Addendum to Vol. VII, p. 93.—More recent analyses by Smetham of a great variety of vegetable feeding stuffs are given in "*The Analyst*," 1914, 39, 481; *J. Soc. Chem. Ind.*, 1914, p. 1107.

#### ERRATUM IN VOL. VII.

Page 104, line 9, "122.9°" should read "—122.9°."

<sup>1</sup> *Analyst*, 1914, 39, 519.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1914, 36, 759.

# PROTEINS OF MILK.

By L. L. VAN SLYKE.

**Method of Preparing Ash-free Casein.**—The method described on pages 116–117, Vol. VIII, is modified as follows by Van Slyke and Bosworth:<sup>1</sup> After the casein has been precipitated and redissolved four or more times, the final solution in dilute ammonia is treated with 10 c.c. of strong ammonia and then with 20 c.c. of saturated solution of ammonium oxalate. The mixture is allowed to stand 12 hours or more. The precipitated calcium oxalate is removed by centrifugal force and subsequently by filtering through a double thickness of filter paper. The filtered solution is next treated with dilute hydrochloric acid (10 c.c. acid, sp. gr. 1.20, diluted to 1 litre) until the casein is precipitated. The precipitate is washed with distilled water until free from chlorides and is then placed on a hardened filter paper in a Buchner funnel, as much water as possible being removed by suction. The mass is next transferred to a large mortar and triturated thoroughly with 95% alcohol and, after its removal by suction, again triturated with absolute alcohol; after filtering by suction, the mass is twice treated with ether, which is removed each time by suction. The material is then spread out in a thin layer and allowed to dry in a warm place for 12 hours. It is finally ground in a mortar so as to pass a 40-mesh sieve and dried for 2 days over sulphuric acid under diminished pressure. Such preparations were found to contain less than 0.10% ash. The phosphorus content of such preparations is about 0.70% instead of 0.85%, the amount obtained with casein made under ordinary conditions without the removal of the calcium.<sup>2</sup>

**Compounds of Casein and Paracasein with Bases.**—The existence of caseinates and paracaseinates in addition to those containing 1.50% and 2.50% of CaO has been shown.<sup>3</sup> Compounds of casein with K, Na, NH<sub>4</sub>, Mg, Ca, Sr and Ba have been prepared; the general results are shown in the following table:

Basic elements	Mono-basic compounds of casein; 100 grm. of casein combine with, grm.	Di-basic compounds of casein; 100 grm. of casein combine with, grm.
NH <sub>4</sub> .....	0.20	....
Na.....	0.26	....
K.....	0.44	....
Mg.....	0.13	0.24
Ca.....	0.22	0.44
Sr.....	0.48	0.96
Ba.....	0.76	1.51

<sup>1</sup> *J. Biol. Chem.*, 1913, 14, 203.

<sup>2</sup> Bosworth and Van Slyke, *J. Biol. Chem.*, 1914, 19, 67.

<sup>3</sup> Van Slyke and Bosworth, *J. Biol. Chem.*, 1913, 14, 211, and Van Slyke and Winter, *ibid.*, 1914, 17, 287–291.

Corresponding paracaseinates have been prepared, but they contain twice the amount of base contained in the caseinates. Mono-basic caseinates and paracaseinates of ammonium, sodium and potassium are soluble in water, but those of magnesium, calcium, strontium and barium are insoluble in water but are soluble in warm 5% solutions of sodium, ammonium and potassium chlorides. The solubility is due to an exchange of bases; the action, for example, between mono-calcium caseinate and sodium chloride results in the formation of the soluble sodium caseinate and calcium chloride. The action is reversible. Di-basic caseinates are soluble in water and are easily precipitated by soluble salts of calcium, strontium, barium, etc.

**Molecular Weights and Valency of Casein and Paracasein.**—On the basis of the analytical results obtained in studying the composition of the mono-basic and di-basic caseinates and paracaseinates, together with other facts, Van Slyke and Bosworth<sup>1</sup> have concluded that the molecular weight of casein is 8888 and that of paracasein 4444; and also that the valency of the protein molecule in basic caseinates is 8, in basic paracaseinates, 4.

**Estimation of Casein.**—Richmond's method for the estimation of total proteins in milk by means of formaldehyde<sup>2</sup> has been adapted by Walker<sup>3</sup> to estimate casein in milk. To 10 c.c. of milk is added about 1 c.c. of a 1% solution of phenolphthalein and then *N*/9 solution of sodium hydroxide is added with constant stirring until a fairly deep pink colour appears and remains. No account is kept of the amount of alkali thus used. Then about 2 c.c. of neutral 40% formaldehyde solution is added, when the pink colour disappears. The reading of the burette is now recorded and alkali is again added with stirring until the same intensity of colour results as in the first titration. The reading of the burette is again taken and the difference between the two readings gives the number of c.c. of alkali used in the second titration, and this figure multiplied by 1.63 gives the percentage of casein in the milk.

If a sample of 16.3 c.c. of milk is used, the reading of the burette gives the percentage of casein directly without multiplying by the factor 1.63. Solution of *N*/10 alkali can be used provided a 9 c.c. sample of milk is taken for the estimation, the final result being multiplied by 1.63.

The formaldehyde solution is kept neutral by adding a few drops of phenolphthalein to the formaldehyde solution in the bottle and then alkali until a pink colour remains.

The results obtained show excellent agreement with the A. O. A. C. method.

<sup>1</sup> *J. Biol. Chem.*, 1913, 14, 227 and 231.

<sup>2</sup> *Analyst*, 1911, 36, 9.

<sup>3</sup> *J. Ind. Eng. Chem.*, 1914, 6, 131.

# MILK PRODUCTS.

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By CECIL REVIS AND E. RICHARDS BOLTON.

**Regulations in England, Local Government Board, Oct., 1912** (cf. Vol. VIII, p. 184).—Preserved cream is defined as cream having not less than 35% of milk fat by weight, and to which has been added (1) boric acid, borax or a mixture of these substances, or (2) hydrogen peroxide.

No thickening substance is to be added to cream, whether preserved or not.

No other preservative than those specified above may be used.

Cane sugar and beet sugar are not regarded as either preservatives or thickening agents. Calcium saccharate is forbidden.

All preserved cream must be labelled in accordance with the nature of the preservative.

The above regulations have led to considerable trouble since, though preservatives are allowed, the maximum quantity to be used is not specified, and it is left to individuals to settle what amount may be considered prejudicial to the public health.

In many cases the maximum has been placed at 0.25% calculated as boric acid ( $H_3BO_3$ ), but this is not really sufficient in warm weather for trade purposes, and 0.35% at least should be allowed.

**Regulations as to Preservatives in Food made by Canadian Order-in-Council, April 4, 1914.**—The following preservatives are allowed in the quantities shown, unless satisfactory evidence of harmfulness shall be forthcoming. Only one preservative of any kind is allowed in any kind of food product, or in a mixture of two or three kinds of food:

(1) Boric acid. Limit, 1 part in 400 for cream, 1 part in 200 for butter and other foods.

(2) Benzoic acid (sodium benzoate). Limit, 1 part in 1,000 parts.

(3) Salicylic acid. Limit, 1 part in 5,000 parts.

(4) Sulphurous acid (bisulphite of soda, potash or lime). Limit, 1 part in 2,000 for solid foods.

(5) Saccharin. Limit, 1 part in 700 parts for solid foods.

The following preservatives are completely prohibited: formaldehyde (formalin),  $\beta$ -naphthol, abrastol (asaprol) hydrofluoric acid, fluorides, fluo-borates, fluo-silicates, or other fluorine compounds.

**Estimation of Sugars in Condensed Milk** (cf. Vol. VIII, p. 213).—A careful investigation has recently been made by Revis and Payne<sup>1</sup> into the inversion factor to be used when acid mercuric nitrate is employed as

<sup>1</sup> *Analyst*, 1914, 39, 476.



coagulant and inversion agent for condensed milk. Not only does acid mercuric nitrate immediately commence to invert cane sugar but, as Richmond has shown, the precipitation of protein is not complete, the small quantity left having quite an appreciable effect on the readings. The new factor proposed by them obviates these sources of error.

In order to avoid the use of special measuring vessels graduated at novel temperatures, which are not likely to be in the ordinary laboratory, they have adopted the following procedure:

65.085 grm. of the condensed milk are weighed out and washed into a graduated flask containing 250 true c.c. adjusted at 15° C. (the ordinary standard Charlottenburg flask), with sufficient water to bring the volume to about 220 c.c. This is then heated in boiling water for 5-10 minutes, or else allowed to stand over night. In either case, the volume is eventually made up to the mark at 15° C. After well mixing, 100 c.c. are measured out into a long stoppered cylinder with a 50 c.c. pipette (50 c.c. = 50 grm. of water at 15° C.), 10 c.c. (true c.c. at 15° C.) of acid mercuric nitrate added and the whole violently shaken for 30 seconds till the curd is in the finest possible state of division. The cylinder is allowed to stand for 5 minutes at 15° C. and the contents then filtered through a dry filter. As soon as sufficient for the direct reading has passed, its temperature is raised to 20° and the tube filled and the reading taken at that temperature. 25 c.c. of the remainder of the filtrate are placed in a 50 c.c. stoppered flask, counterpoised, and then heated in boiling water for 8 minutes, cooled, readjusted to the original weight, filtered, if necessary, and the invert reading taken as near 20° as possible.

The readings are corrected for the increase in volume due to the added mercuric nitrate less the volume of the fat (F) and protein (P) precipitated.

This correction (C) will be,

$$C = 10 - \left\{ \frac{(F \times 1.11) + (P \times 0.82)}{100} \times 26.034 \right\}$$

and the readings must be multiplied by (100 + C) to give the correct results for the normal weight. The following formulæ then give the percentage of sugars.

$$\text{Cane sugar } \% = \frac{(D - I)100}{R_c - \frac{T}{2}} = S$$

$$\text{Lactose (anhydrous) } \% = (D - S) \times \frac{R_L}{26.034} \times 100$$

there D = corrected direct reading.

I = corrected invert reading.

$R_c =$   
 $R_L =$  } the inversion and lactose factors.

T = temperature of invert reading.

It is assumed that a Schmidt and Haensch quartz wedge compensating polarimeter is used, reading in saccharose units, and so graduated that when 26.048 grm. of saccharose are dissolved in 100 Mohr c.c. at 17.5° C. and polarised at 17.5° C. the reading is 100 scale divisions.

The change in the above formulæ of 26.048 to 26.034 is necessitated by the analytical procedure adopted.

As the result of many careful experiments the following values were obtained for  $R_c$  and  $R_L$  at sugar concentrations such as will be realised in dealing with condensed milk:

$$R_c = 141.71$$

$$R_L = 0.3086$$

**Aldehyde Figure for Cream** (Vol. VIII, p. 187).—Richmond<sup>1</sup> has pointed out that a determination of the aldehyde figure for cream will at once show whether a low fat percentage is due to the addition of milk or water.

The aldehyde figure for cream devoid of fat is practically identical with that of skim milk, so that the addition of milk to cream has no effect on the aldehyde figure calculated on the cream devoid of fat, whilst the addition of water naturally at once lowers it.

The aldehyde figure is determined in the usual way (Vol. VIII, p. 154) and calculated to c.c. of  $N/1$  strontium or sodium hydroxide per 1,000 c.c. of cream. This figure is then calculated to cream devoid of fat thus:

$$\text{Aldehyde figure} \times \frac{100}{100 - \text{fat}}$$

The average figure for cream is 20.8 c.c., using  $N/10$  strontium hydroxide for the titration. If  $N/10$  sodium hydroxide be used the figure becomes 15.8° c.c. If the figure obtained is distinctly below 20.8 c.c. (or 15.8 c.c. for sodium hydroxide) the addition of water is indicated.

The above considerations also bear out the contention of Richmond that the solids not fat of cream are in the same ratio to the water present as they are in milk.

In determining the aldehyde figure, Richmond has suggested the use of a standard pink colour for the detection of end points. The standard tint is made by adding to 10 c.c. of milk 1 drop of 0.01% solution of rosaniline acetate in 96% alcohol.

It follows that the acidities determined in this manner will be slightly higher (about 1.5°) than those obtained in the usual manner by titrating till the first pink tinge is observed to be permanent, but the titration for the aldehyde figure, which is a difference only, is not affected and is probably rendered more accurate as the sensitiveness of the observer's eye to a pink colour varies in different individuals.

**Gerber Method** (Vol. VIII, p. 187).—In order to simplify the introduction of the cream into an ordinary Gerber tube, Bracher uses a small

<sup>1</sup> *Analyst*, 1914, 39, 243.

glass cup fitted by a solid glass stem into the India-rubber stopper of the tube, similar to those supplied with the special Gerber tube open at each end. The cup is made sufficiently wide to pass into the opening of an ordinary Gerber "bottle" and has a capacity of about 1.25 c.c. This allows about 1 grm. of all creams to be weighed into it. The acid is run into the bottle, followed by 10 c.c. of water and 1 c.c. of amyl alcohol, and then the stopper and cup carefully inserted. The narrow bore of the cup prevents the cream from running out. The test is finished in the usual manner.

**Analysis of Dried Milks** (Vol. VIII, p. 239).—An extensive investigation into the methods of fat estimation in dried milk has been made by Utz.<sup>1</sup> His conclusions are similar to those arrived at for cheese, and he recommends the Polenske method (see cheese) as the best and quickest. The following analyses are also due to him:

Description	Water	Ash	Fat	Protein, N×6.37	Sugar, (by diff.)
Whole milk.....	7.28	5.44	27.72	24.33	35.23
Whole milk.....	4.14	4.94	37.50	21.40	32.03
Whole milk.....	7.19	5.65	27.41	25.54	34.21
Whole milk.....	6.43	5.38	29.71	24.33	34.15
Whole milk.....	6.33	5.23	26.50	24.97	36.97
Half cream milk.....	7.31	5.85	20.30	27.65	38.89
Half cream milk.....	8.00	6.26	14.80	28.99	41.95
Half cream milk.....	6.69	6.26	14.65	28.54	43.86
Skim milk.....	9.04	6.96	1.07	30.58	52.35
Skim milk.....	10.31	7.14	1.92	32.81	47.82
Skim milk.....	9.05	6.87	0.63	33.25	50.20
Cream.....	3.65	3.96	51.37	17.65	23.37
Cream.....	4.17	4.21	43.80	18.98	28.84

These are all probably of German origin.

Analysis of Cheese.

**Fat Estimation.**—Considerable attention has been given during the last year or two to the analysis of cheese particularly as to its fat content. In order to ensure uniformity of results this question has been fully investigated by several workers, particularly by Utz<sup>2</sup> who considers that the best methods are (1) the Ratzliff-Schmid-Bondzynski and (2) the Polenske.

(1) **The Ratzliff-Schmid-Bondzynski Method.**—3–5 grm. of cheese are placed in a flask with 10 c.c. of hydrochloric acid (sp. gr. 1.125) and boiled gently over a small flame for 8–10 minutes. The solution is cooled and poured into a Gottlieb tube, 25 c.c. of methylated and petroleum ethers respectively added, in that order, mixing the solution gently by inversion after each addition. The ethereal layer is allowed to separate for 6 hours, pipetted off into a weighed flask and the acid liquor extracted once more with the same volume of ethers. The ether in the weighed flask is then distilled off and the fat dried to constant weight.

(2) **The Polenske Method.**—1–1.5 grm. of cheese are placed in a conical flask with 10 c.c. of water and 5 c.c. sulphuric acid (sp. gr. 1.81–1.84) and the mixture heated over a small flame, being allowed to boil gently for

<sup>1</sup> *Milch Zentralbl.*, 1914, 43, 113.  
<sup>2</sup> *Milch Zentralbl.*, 1913, 42, 457.

2 minutes, a cooling tube being preferably arranged in the mouth of the flask. 35 c.c. of water are then added, the solution cooled, and 50 c.c. of methylated ether (at 18°) run in and the mixture gently shaken. 50 c.c. of petroleum ether (at 18°) are added and the mixture again gently shaken for 1 minute, and then cooled in water at 18°. After 15–20 minutes 49.5 c.c. of the ether are pipetted off and passed through a cotton wool filter into a small weighed flask. The cotton wool is washed two or three times with a little ether, the ether then distilled off and the fat dried and weighed.

The final proposals (April 27, 1913) of the Committee of the Fédération Internationale de Laiterie for the unification of analytical methods for cheese are as follows:

(1) **Estimation of Water.**—2–3 grm. of the mixed sample of cheese are quickly weighed into a suitable flat nickel or platinum dish, containing either ignited coarse quartz powder or sea sand purified by hydrochloric acid, and a glass stirrer, and the cheese mixed with the quartz powder or sea sand as equally as possible. The dish is then heated in an oven at 105–110°.

After about 1½ hours the weight is determined and weighings are made at the expiration of succeeding half hours till the weight ceases to diminish. The weight of the cheese residue is taken as that of the *dry substance*, the loss in weight as the water of the cheese.

(2) **Estimation of Fat.**—(A) *By Gerber's method (with modified cheese butyrometer of Van Gulik) for 3 grm. of cheese.*

(A) *Approximate Method.*—3 grm. of cheese are introduced with the aid of a funnel into the widened part of the cheese butyrometer (Fig. 7) which has previously been half filled with sulphuric acid (sp. gr. 1.50). The weighing of very soft cheese is done in a beaker.

The butyrometer is then warmed in a water-bath at 65–70° and the casein dissolved, shaking and swinging the butyrometer at intervals. When no more particles of cheese are visible the butyrometer is left in the water-bath for a short time, swinging at intervals, and then after 1 c.c. of amyl alcohol has been added, it is filled with sulphuric acid nearly up to the mark 35. The contents are mixed with care, not swinging (or shaking) the butyrometer more than necessary to ensure complete mixing, then left for about 5 minutes in the water-bath and whirled at a speed of 1,000 rotations per minute. The diameter of the disc-plate of the Gerber centrifugal machine must be at least 47 cm. (the machine should be warmed when the temperature of the room is low). Finally the butyrometer is placed in a water-bath for 5 minutes at 65° and the height of the fatty layer read at 65°.

(B) *Hydrochloric Acid Method.—Final Method.*—1–5 grm.<sup>1</sup> of rasped cheese are gently boiled with 20 c.c. of hydrochloric acid (sp. gr. 1.13) in a small flask, shaking until all small particles have disappeared.

<sup>1</sup> In applying this method it is advisable to use, within these limits, a smaller quantity of fat cheese and a larger one of skim milk cheese.

Then either: (1) *Smetham's percolation method* or (2) the *modified Schmid-Bondzynski method* is applied.

(1) *Smetham's Percolation Method*.—The hydrochloric acid solution, when cool, is carefully introduced into the flask of a Smetham's extractor (Fig. 18), as modified for the estimation of fat in milk, and the flask filled with ether until it flows over.

After extraction for 2 hours the ether is evaporated and the fat dried for half an hour in the oven at 102°. Drying is continued to constant weight.

FIG. 17.—Butyrometer, Gerber-Van Gulik. ( $\frac{1}{2}$  actual size.)

FIG. 18.—Smetham's flask. ( $\frac{1}{2}$  actual size.)

For control a second flask can be connected to the extractor and treated as above.

(2) *Modified Schmid-Bondzynski Method*.—The hydrochloric acid solution is carefully introduced into a 100 c.c. cylinder and, when cool, ether is added until the total volume is about 50 c.c. The cylinder is closed with a damped cork, well shaken, and left for at least 2 hours for the two liquids to separate completely. The ether-fat solution is then drawn off as completely as possible (to at least 1 c.c.) into a weighed flask. A fresh quantity

of 50 c.c. ether is introduced into the cylinder and the contents swung several times. After standing 1 hour the ether is again drawn off as completely as possible and added to the first ether-fat solution in the weighed flask.

The ether is then distilled off and the fat dried for half an hour in the oven at 102°.

Drying is continued to constant weight.

#### ERRATUM IN VOL. VIII.

Page. 188. The percentage of added water in cream is better given by the following formula:

$$\text{Per cent. added water} = \frac{100f + 950 - 110t}{0.95t - f}$$

# ALBUMINOIDS.

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By JEROME ALEXANDER.

W. Bachman<sup>1</sup> has investigated the ultramicroscopic structure of jellies with the slit and cardioid ultramicroscopes.

In the case of 1-2% solutions of gelatin, optically homogeneous except for dust particles and similar impurities, the course of gelatinisation exhibited six different phases: (1) a homogeneous light-cone, linearly polarised; (2) a scintillating motion, which gradually resolved into (3) a dense mass of submicrons with a translatory motion; (4) diminution of the Brownian movement of the optical impurities of the gelatin solution; (5) diminution of the translatory motion of the gelatin submicrons and oscillatory motion about a mean position of equilibrium; (6) a differentiated gel with quiescent "jelly elements" (*i.e.*, the smallest structural elements detectable by ultramicroscopic means), which because of their strong linear polarisation of light, are probably aggregations of submicrons and amicrons. The mass of the gel is resolved into ultramicroscopic and microscopic elements, which, in the order of their magnitude, lie near the limit of the power of resolvability of the microscope; these elements may be microscopic in one dimension and ultramicroscopic in another.

Increasing concentration renders the ultramicroscopic heterogeneity of the jellies less and less distinct; jellies of 7-10% concentration appear homogeneous, but the strong polarisation of the diffuse light cone indicates that they are actually heterogeneous and probably composed of extremely fine particles formed into larger jelly elements. The more concentrated the jelly, the closer together these "jelly elements" would be, and the smaller would be their difference in composition and therefore in refractive power between the two phases, so that at a certain concentration the two phases would be indistinguishable even with the ultramicroscope, *i.e.*, the jelly would appear homogeneous. In the case of gelatin solutions of such small concentration that they do not gelatinise (0.5%) flocks are gradually formed owing to the aggregation of isolated "jelly elements" or of submicrons.

The observations in all cases indicate a very much finer structure for jellies than that described by Bütschli. Jellies treated with alcohol or chromic acid showed under the microscope the honeycomb structure of Bütschli, but the structure revealed by the ultramicroscope was a granular ("globulitic") one; and it was found that the alcohol (or chromic acid)

<sup>1</sup> *Zeit. anorg. Chem.*, 1911, 73, 125-172.



caused coagulation and shrinking (dehydration) and that these are the cause of the honeycomb structure of Bütschli, the true structure of the jelly being much finer.<sup>1</sup>

For the *detection of glue* in sizing materials E. Schmidt (*Farber Ztg.*, 24, 97-98) uses ammonium molybdate and a modified Nessler's solution, which he finds more sensitive than the biuret test or precipitation with tannin. The special Nessler solution is prepared by making ordinary Nessler solution slightly acid with sulphuric acid, and filtering to remove the red precipitate. The clear yellow filtrate is a sensitive test for glue even in the presence of ammonium salts.

Both of these reagents give a faint turbidity with a solution containing 0.00001 grm. glue in 5 c.c. water. Norgine and albumin interfere with the test, and must be removed by adding dilute nitric acid to the solution, freed from fat, and then filtering.

**Detection of Gelatin.**—The provisional method adopted by the U. S. Dept. of Agriculture<sup>2</sup> for the detection of gelatin consists in shaking 10 c.c. of the cream with 10 c.c. of acid mercuric nitrate solution, filtering after 5 minutes, and adding an equal volume of picric acid solution; a precipitate is produced if gelatin is present. G. E. Patrick<sup>3</sup> pointed out that sour cream containing no gelatin frequently gives the above reaction, because of the presence of "pseudo-gelatin" decomposition products. A. Seidenberg<sup>4</sup> found that the two precipitates may be differentiated by the fact that while both precipitates are soluble on heating in slightly acid solutions, only the "gelatin picrate" is soluble in hot neutral water alone. The picric acid precipitate from sour cream appears to be entirely insoluble in hot water, after all the picric or other acid has been removed. To accomplish this, the picric acid precipitate is shaken vigorously to cause it to coalesce, and after standing, most of the liquid can be siphoned off. The precipitate is washed on a filter with water containing 2 or 3 drops of ammonium hydroxide to 100 c.c., until the washings are slightly alkaline to litmus; it is then boiled with 10-20 c.c. of distilled water and filtered hot into a test-tube. If gelatin is present, the cooled filtrate will give a decided precipitate with an equal volume of picric acid solution. By this method it is possible to detect 0.5% of gelatin in 20-25 c.c. of sour cream.

To separate gelatin from an aqueous solution containing proteins, albumoses, peptones, mucin and casein, Berrár<sup>5</sup> adds to the solution about 2 volumes of a mixture of 1 part of a saturated aqueous solution of picric acid with 4 parts of 96% alcohol. The gelatin alone remains in solution, and after filtration may be quantitatively precipitated by adding about 1½ volumes of saturated aqueous picric acid solution and allowing the mixture to stand for 12 hours at 10°. By this means he accurately estimated

<sup>1</sup> See also R. Zeigmondy, *Zeit. anorg. Chem.*, 1911, 71, 356-377.

<sup>2</sup> *Bull.* 107, rev., 121.

<sup>3</sup> U. S. Dept. Agr., *Bull.* 116, p. 24.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1913, 5, 927.

<sup>5</sup> *Biochem. Zeits.*, 1912, 47, 189-214.

gelatin mixed with milk and egg albumin. The gelatin picric-acid precipitate was washed with a solution of potassium mercuric iodide until the washings were no longer yellow in colour; the quantity of gelatin in the residue was found by estimating the nitrogen content.

For the qualitative detection of gelatin in the presence of proteins, the filtrate from the alcohol-aqueous picric-acid solution, is tested with picric acid solution, a yellowish-white opalescence being formed even at a concentration of 1 in 100,000. The opalescence is best detected by a "ring-test."

Berrár also found that the solubility of purified gelatin in cold water is 0.56, 0.60 and 0.62% at temperatures of 17°, 18° and 19° respectively. These concentrations approximate to the minimum required for the formation of a jelly; thus a 0.7% solution in hot water sets to a thin jelly on cooling. If a saturated solution, formed in the cold, remains in contact with pieces of gelatin, a partial separation of the dissolved substance occurs upon further cooling, but no gelatinisation. Neither alcohol nor metaphosphoric acid precipitates gelatin completely from aqueous solutions. The same is true of picric acid at ordinary temperature, but at 8° complete precipitation occurs on adding an equal volume of saturated aqueous picric acid solution. When gelatin is completely precipitated by acid reagents, *e.g.*, by a solution containing picric acid and potassium mercuric iodide (the precipitate may in this case be safely washed with water) the gelatin and acid combine in definite proportions, 1 molecular equivalent of acid combining with a quantity of gelatin containing 10 atoms of nitrogen. On the assumption that 1 molecular equivalent of acid unites with 1 molecule of gelatin, the molecular weight of the latter must be 823 (Paal found 900).

The nitrogen content of picric acid or of precipitates containing this compound and proteins or gelatin, may be estimated accurately by a modification of the Kjeldahl method. The material is treated in a Kjeldahl flask, with 0.5–1 gm. of iron filings, 5 c.c. of glacial acetic acid, 20 c.c. of concentrated sulphuric and some copper sulphate; the mixture is heated in the ordinary way, and the subsequent operations carried out as usual.

To replace hide powder in tannin analysis, E. Giusiana<sup>1</sup> proposes the use of fish glue or gelatin previously tanned in a basic chrome solution prepared from 100 gm. of chrome alum crystals, 1,000 c.c. of water and 15 gm. of crystallised sodium carbonate. After soaking for 24 hours in this solution, thin sheets of gelatin are completely tanned and are quite insoluble in hot water. They are washed, neutralised in 1% ammonia, again thoroughly washed and dried between filter papers. The tanned gelatin may be kept indefinitely in distilled water. For 100 c.c. tannin solution the equivalent of 5 gm. of dry gelatin is used. The shakings, filtrations, etc., are the same as in the hide powder process.

<sup>1</sup> *J. Am. Leather Chem. Assoc.*, 1913, 8, 143.

# MEAT AND MEAT PRODUCTS.

By JOHN PHILLIPS STREET.

## MUSCLE EXTRACTIVES.

**Glycogen.**—Trowbridge and Francis<sup>1</sup> obtained the following percentages of glycogen in beef liver and lean beef muscle:

Description of animal	Glycogen in liver	Glycogen in lean muscle
	%	%
	Slaughtered 2-3 hours after regular A.M. feed	
Very fat Short-horn, 4½ years.....	3.803	0.663
Lean Jersey cow, 6 years.....	2.337	0.697
Fairly fat Short-horn, 3½ years. ....	1.210	0.243
Fat yearling Hereford .....	0.927	0.375
Fat Hereford, 20 months.....	0.820	0.309
	Slaughtered 5-6 hours after regular A.M. feed	
Thin Hereford, 2 years.....	0.965	0.569
Very thin Hereford, 23 months.....	0.913	0.416
Thin Hereford, 11 months.....	0.625	0.158
	Slaughtered 9 hours after regular A.M. feed	
Very fat Hereford, 3 years.....	1.160	.....
Fairly fat Hereford, 18 months.....	0.284	0.140

The above data show the greater tendency of older animals to store glycogen and the influence of the length of time elapsing after feeding before the animal is slaughtered on the amount of glycogen that remains stored in the organs and muscles. Furthermore, the glycogen-content of the muscle of the emaciated Hereford steer (0.416%) shows that notwithstanding this emaciated condition, and the fact that the entire carcass contained no fat which could be separated mechanically, the muscle still contained glycogen in considerable quantity.

Trowbridge and Francis also obtained (*loc. cit.*) the following percentages of glycogen in cow liver and horse flesh at various periods of time after slaughter.

Liver of cow	Glycogen	Horse flesh	Glycogen
	%		%
After 2 hours 13 minutes	3.13	After 36 minutes.....	0.146
After 1 week.....	2.67	After 22 hours.....	0.072
After 15 days.....	2.34	After 3 days.....	0.013

These experiments show that the glycogen-content of beef muscle and beef liver ranges from 0.1 to 0.7, and from 0.2 to 3.8%, respectively; that starvation or extreme debility does not cause complete removal of glycogen from the muscle or liver; that the glycogen slowly decreases, but does not entirely disappear when the meat is kept at a temperature of 6.5° C. for over

<sup>1</sup> *J. Ind. Eng. Chem.*, 1910, 2, 215.

two weeks; that glycogen may be present even when the liver is unfit for food; that horse flesh is subject to an enzymatic hydrolysis of the glycogen similar to that of beef; and finally that the glycogen content cannot be said to offer an absolute or even approximate basis for distinguishing beef from horse flesh.

**Estimation of Glycogen.**—Starkenstein<sup>1</sup> calls attention to a source of error in Pflüger's method. Ferric hydroxide, which may be present, is capable of absorbing large quantities of glycogen. The insoluble portion obtained after treating the tissue with potassium hydroxide should be dissolved in hydrochloric acid and the glycogen estimated in the solution. Unless this is done the error may amount to as much as 50% of the total glycogen present.

Bierry and Gruzewska<sup>2</sup> suggest the following method, which they claim gives excellent results:

Place 25 grm. of finely hashed meat in a flask containing 25 c.c. of potassium hydroxide solution. Heat for 15 minutes till the tissue is completely dissolved, then in an autoclave at 100° for 30 minutes. Cool, neutralise to litmus with hydrochloric acid, make up to 100 c.c., and heat in an autoclave at 120° for 30 minutes. Cool and neutralise with sodium hydroxide. Precipitate the proteins with mercuric nitrate. Filter the liquid brought up to 300 c.c. with the wash water and add zinc powder to remove excess of mercury. After several hours a colourless liquid is obtained. Estimate the dextrose in a 10 c.c. aliquot and multiply by 0.927 to obtain the weight of glycogen.

**Estimation of Lactic Acid.**—Meissner<sup>3</sup> concentrates the lactate solution to a syrup, then treats with 5 c.c. of phosphoric acid and rubs with dry calcium sulphate to form a powder. This is extracted with ether for 7–9 hours, thus removing the lactic acid quantitatively. The extract is concentrated and the acid titrated, or estimated as carbon monoxide by conversion into the barium salt, concentrating to dryness and decomposing with sulphuric acid in an atmosphere of carbon dioxide. The decomposition is usually complete at 100°, but the flask may be heated to the boiling point of sulphuric acid.

Yoshikawa<sup>4</sup> estimates *d*-lactic acid by measuring the rotation of its lithium salt.

**Detection of Inositol.**—All of the inositols upon oxidation with nitric acid yield coloured oxyquinone derivatives. In carrying out this test Scherer's method<sup>5</sup> is generally used. Treat a small amount of the material to be tested with a little nitric acid and evaporate on a water-bath almost to dryness; add a little ammoniacal barium chloride or calcium chloride, and again evaporate the solution. If inositol is present, a beautiful rose-red colour will develop; 0.5 mg. of inositol may be detected.

<sup>1</sup> *Biochem. Zeit.*, 1910, 27, 53.

<sup>2</sup> *Compt. rend.*, 1913, 156, 1491.

<sup>3</sup> *Biochem. Zeit.*, 1915, 68, 175.

<sup>4</sup> *Zeit. physiol. Chem.*, 1913, 87, 382.

<sup>5</sup> *Liebig's Ann.*, 1850, 73, 322; 1852, 81, 375.

Seidl<sup>1</sup> has modified the test by using ammoniacal strontium acetate to develop the colour and in this way 0.3 mg. may be detected.

Salkowski<sup>2</sup> has still further modified the Scherer test as follows: Dissolve a small amount of the substance in 1-2 drops of nitric acid, add a few drops of 10% calcium chloride solution, then a few drops of 1-2% platinic chloride solution, and evaporate the whole in a porcelain dish. The presence of inositol is indicated by a rose-red to brick-red colour, the test being sensitive to 0.1 mg.

### Nitrogenous Muscle Extractives.

**Occurrence.**—Wilson<sup>3</sup> has reviewed in detail the work of recent years on the nitrogenous extractives of muscle. The following is a summary of the various nitrogenous compounds thus far found in the muscular tissue of both vertebrate and invertebrate animals:

**Amino-acids.**—*Alanine.*—In beef extracts and the muscle of lobster, salmon, tunny, snapper, crab and dried codfish.

*Glycocoll.*—In scallop, mussel, crab extract and shell fish; none in octopus.

*Glutamic Acid.*—In beef extract and dried codfish.

*Leucine.*—In crustacea, cephalopods, spiders and insects; specifically in crab extract, lobster, cuttlefish, sardines and crab.

*Tyrosine.*—In crab extract, lobster, sardines, snapper, crab and many invertebrates.

*Histidine.*—In beef extract, bonito, tunny, salmon and sardines.

*Arginine.*—In crab extract, lobster, crab and clam.

*Lysine.*—In crab extract and lobster.

*Proline.*—In lobster.

*Tryptophane.*—In crab.

*Taurine.*—In oyster, cuttlefish, octopus, frog, alligator, cephalopods, mollusca, periwinkle, abalone, beef extract and dried codfish.

**Dipeptides.**—*Anhydride of d-alanyl-d-alanine.* In beef extract.

*Carnosine (Ignotine).*—In beef extract, muscles of ox, bonito, tunny, salmon, eel, calf, rabbit, sardine, horse and pig. None found in liver or kidney extracts. Several investigators have failed to obtain it from invertebrate muscle.

*Methylguanidine.*—In beef extract and muscle of ox, haddock, calf, horse and codfish. It has been found in liver extract but not in kidney extract.

*Creatine and Creatinine.*—In the muscle of practically all vertebrates.

*Trimethylamine.*—In fish and invertebrate extracts. It is possibly present only in small amounts in living muscle.

*Choline.*—In beef extract, crab extract, dogfish and in many plant and animal tissues.

<sup>1</sup> *Chem. Zeit.*, 1887, 11, 676.

<sup>2</sup> *Zeit. physiol. Chem.*, 1910, 69, 478.

<sup>3</sup> *Chemistry of the Nitrogenous Extractives of Muscle Tissues*, Thesis, Yale Univ., 1914.

*Neurine*.—In beef extract and haddock.

*Carnomuscarine*.—In beef extract.

*Betaine*.—In sugar beet and many plant and animal extracts; also in muscle extracts of shrimp, crab, oyster, clam, dogfish, cuttlefish, octopus, mussel, dried codfish, scallop, periwinkle and lamprey.

*Neosine*.—In beef extract, crab extract and ox muscle.

*Carnitine*.—In beef extract and muscle of ox, calf, horse and pig; not in kidney or liver extracts.

*Myokynine*.—In dog and horse.

*Oblitine*.—In beef extract.

**Purines**.—*Hypoxanthine, xanthine, guanine and uric acid*. In muscle extracts.

*Carnine*.—In beef extract and horse muscle.

*Inosinic acid*.—In beef extract.

**Miscellaneous Compounds**.—*Methylamine*. In flesh of coot.

*Iminazolethylamine*.—In tunny.

*Urea*.—Probably present in small amount in all muscle extracts. Unusually large amounts in muscle extracts of cartilaginous fishes.

**Compounds of Unknown Structure**.—*Vitiatine and Creatosine*.—In beef extract.

*Canirine*.—In crabs and snapper.

*Crangitine and Crangonine*.—In crab extract.

*Melolonthine*.—In cockchafer.

Wilson gives in his thesis an extensive bibliography of muscle extractives. The reader is also referred to the papers by Ackermann, Becker, Blaha, Bottazzi, Buglia and Constantino, Cabella, Demjanowski, Dietrich, Einbeck, v. Fürth, Gulewitsch, Jansen, Jona, Krimberg and Israilsky, Mauthner, Mendel, Micko, Myers and Fine, Smorodinzew, Suzuki, Wilson and Yoshimura, which have appeared during the last three years, chiefly in *Zeit. physiol. Chem.*, *J. Biol. Chem.*, *Biochem. Zeit.*, and *Amer. J. Physiol.*

### Estimation of Nitrogenous Extractives.

**Creatine and Creatinine**.—The Folin method with its various modifications continues to be the standard method for determining these meat bases. Wieland<sup>1</sup> has pointed out that the salts of acetic acid, semi-carbazide, dioxyguanidine and quinol give a red colour with picric acid and soda. Sudendorf and Lahrmann<sup>2</sup> have made a similar observation, and have modified the method by using a 1% solution of potassium permanganate, which removes the interfering substances. After this treatment tomato juice, yeast extract, caramel and acetone did not give the Jaffé reaction.

Thompson, Wallace and Clotworthy<sup>3</sup> recommend creatinine picrate or

<sup>1</sup> *Konserven-Zeit.*, 14, 249.

<sup>2</sup> *Zeit. Nahr. Genussm.*, 1915, 29, 1.

<sup>3</sup> *Biochem. Jour.*, 1913, 7, 445.



the double picrate of creatinine and potassium for control of the standard dichromate solution in the Folin method. In estimating creatinine in weak solutions, the best results were obtained by using an equal quantity of  $N/1$  hydrochloric acid, and heating either on the water-bath for 3 hours or in the autoclave for 25 minutes at  $117^{\circ}$  C. (identical results were obtained by both methods of heating). The optimum time and temperature for the development of the colour were 7 minutes and  $15-17^{\circ}$  C. For accurate work the readings on the colour scale are strictly proportional only if they lie between limits of 7 and 9 mm. Dextrose to the extent of 10% does not affect the estimation of creatinine.<sup>1</sup>

Folin himself has discarded potassium dichromate as the colour standard, preferring creatinine zinc chloride. His own most recent modification of the method of estimating creatine in muscle is as follows: Transfer 5 gm. of comminuted muscle to a 200 c.c. Erlenmeyer flask and add 100 c.c. of  $N/2$  sulphuric acid. Cover the flask with tin foil and heat in the autoclave at  $130-135^{\circ}$  for 30-40 minutes. After cooling to below  $100^{\circ}$  open the autoclave, cool the contents of the flask and transfer to a 200 c.c. flask. Shake for a short time to break up the skeletal tissues, dilute to 200 c.c. and mix well. Filter and titrate 10 c.c. of the filtrate with 10% sodium hydroxide using phenolphthalein as indicator. To another 10 c.c. portion in a 100 c.c. flask add 20 c.c. of saturated picric acid and enough sodium hydroxide solution to give 1.5 c.c. in excess of that required to neutralise the sulphuric acid. As standards use a solution containing creatinine equivalent to 1 mg. of creatine per c.c. (1.389 gm. creatinine zinc chloride) for striated muscle, and standards half as strong for other muscle. In the former case set the standard at 10 mm., in the latter at 20 mm. In either case 4,000 divided by the reading of the unknown in millimeters gives the creatine in milligrams per 100 gm. of muscle.<sup>2</sup> (See also p. 565.)

### Phosphorus Compounds.

Forbes and Keith<sup>3</sup> have published a very extensive (709 pages) review of the literature of phosphorus compounds in animal metabolism, to which the reader is referred. A very complete bibliography is given.

**Inorganic Phosphorus.**—In estimating inorganic phosphorus in meat and eggs, Chapin and Powick<sup>4</sup> extract the inorganic phosphoric acid by using approximately  $N/10$  hydrochloric acid with an excess of picric acid, the estimation being made in aliquots of the filtrate. In case the amount of water in the sample is not known and the volume of the material insoluble in the extracting liquid cannot be neglected, a known amount of potassium iodide may be added as a "marker," and from the concentration of potassium iodide in the extract the degree of dilution by the water in the sample

<sup>1</sup> Cf. also Baur and Trümpler, *Zeit. Nahr. Genussm.*, 1914, 27, 697.

<sup>2</sup> See *J. Biol. Chem.*, 1914, 17, 463-493.

<sup>3</sup> *Ohio Agr. Expt. Stat., Tech. Bull. No. 5*, 1914.

<sup>4</sup> *J. Biol. Chem.*, 1915, 20, 97.



may be calculated. The potassium iodide is estimated by Schirmer's nitrous acid—urea method.<sup>1</sup> The phosphoric acid is first precipitated with magnesia mixture and then as ammonium phosphomolybdate by Lorentz's method. As eggs deteriorate, as judged by physical means, there is a progressive increase in the ratio of inorganic to total phosphorus.

### Tin in Canned Foods.

Baker<sup>2</sup> obtains tin sulphide in the usual way from 100 gm. of canned food (digesting with nitric and sulphuric acids and precipitating with hydrogen sulphide). This is then dissolved in hydrochloric acid with the addition of potassium chlorate; a few pieces of aluminum foil are then added to the boiling solution to eliminate all the chlorine, and the tin is reduced to the metallic state by adding about 1 gm. of aluminum foil, this and subsequent operations being carried out while an atmosphere of carbon dioxide is maintained over the surface of the liquid. The mixture is again heated, the tin dissolving to form stannous chloride and, after the addition of air-free water, the solution is titrated with *N*/100 iodine solution, using starch as indicator.

### Decomposition of Meat.

Ottolenghi<sup>3</sup> has reviewed the methods proposed to trace the ripening of meat and to ascertain when active decomposition begins. Only Sørensen's method<sup>4</sup> of estimating amino-acids and the microscopical examination for bacteria were found to be of practical use, though Chodat's tyrosinase-*p*-cresol reaction and the lowering of the freezing point and the condition of the serum gave reliable results but were too time-consuming and required a too elaborate manipulation. The amount of amino-acids (expressed as N) should not exceed 350 mg. per 100 gm. of fat- and tendon-free meat dried at 70°. Well-kept meat on this basis usually contains 190–320 mg., and meat in incipient state of decomposition 340–700 mg. As marked decomposition approaches, ammonia is formed, which interferes with the estimation, causing low results unless first removed by distillation.

### Estimation of Ammonia.

Folin's method<sup>5</sup> for the determination of ammonia in urine by means of an air current is applicable to the estimation of ammonia in meat foods. The most recent modification of this method<sup>6</sup> is as follows (compare p. 564):

Arrange five vessels in series as follows: (1) A bottle containing sulphuric acid, with a Hopkins safety bulb, to purify the entering air; (2) a litre flask containing 25 gm. of sample, 250 c.c. of water, 5 gm. of sodium chloride and 1 gm. of sodium carbonate (alcohol may be added to prevent foaming);

<sup>1</sup> *Arch. Pharm.*, 1912, 250, 448.

<sup>2</sup> *8th Int. Congr. Appl. Chem.*, 1912, 18, 35.

<sup>3</sup> *Zeit. Nahr. Genussm.*, 1913, 26, 728.

<sup>4</sup> *Biochem. Zeit.*, 1908, 7, 43, 407.

<sup>5</sup> *Zeit. physiol. Chem.*, 1902–03, 37, 161.

<sup>6</sup> *U. S. Dept. Agr., Bur. of Chem.*, 1913, *Circ.* 108, 10.

(3) a 250 c.c. safety flask; (4) a cylinder, fitted with a Folin absorption tube, containing *N*/10 sulphuric acid; (5) a 100 c.c. safety flask. The last flask should be connected with an air pump powerful enough to draw the ammonia over into the standard acid. Alcohol may be substituted almost wholly for the water if the air current is weak. Titrate the standard acid at intervals of an hour until no more ammonia is given off, carrying out a control experiment at the same time. Methyl-red, cochineal or congo red may be used in aqueous solution, methyl-red or cochineal in alcoholic.

Frozen Meat.

Wright<sup>1</sup> has studied the changes in New Zealand lamb and mutton when exposed to temperatures from 2° to 19° F. for periods up to 160 days. A progressive increase was noted in the soluble nitrogen, this increasing from 21.7 to 75.5% after 14 days. The ammoniacal nitrogen rose from 0.8 to 53% of the total nitrogen. Under cold storage a loss of from 2.5 to 3.5% of moisture was observed, with an increase of proteose, peptone and meat bases, and a decrease in coagulable nitrogen, ammoniacal nitrogen remaining unchanged.

Meat Extracts.

In the list of papers given on page 396, Vol. VIII, no reference is made to the extensive investigation of commercial meat extracts made by Street<sup>2</sup> A very complete bibliography of the subject is given in the above report. The following are Street's maximum and minimum values for thirty-five brands of paste and fluid preparations:

	Paste preparations		Fluid preparations	
	Max.	Min.	Max.	Min.
Water.....	36.54	14.79	68.37	42.03
Organic matter.....	77.90	51.56	41.07	19.05
Ash.....	36.28	14.45	21.56	11.28
Petroleum ether extract.....	0.50	0.04	0.62	0.00
Chlorine.....	17.81	2.50	11.44	2.99
— added salt <sup>3</sup> .....	25.05	0.00	15.84	2.02
Phosphoric acid.....	6.22	1.15	2.87	0.88
Potash.....	12.65	2.29	4.81	1.73
Acidity, <sup>4</sup> phenolphthalein.....	14.50	3.74	6.64	2.40
Acidity, <sup>4</sup> litmus.....	9.07	1.90	4.24	1.18
Nitrogen, total.....	10.47	5.02	5.36	1.78
Nitrogen, insoluble.....	0.34	0.00	0.99	0.00
Nitrogen, coagulable.....	0.26	0.00	0.10	0.00
Nitrogen, ammonia.....	0.74	0.13	0.58	0.11
Nitrogen, ppt. by tannin salt.....	7.89	2.93	3.20	0.64
Nitrogen, meat bases.....	4.37	0.63	2.30	0.80
Nitrogen, ppt. by zinc sulphate.....	5.04	0.44	1.59	0.31
Nitrogen, creatinine.....	1.85	0.07	0.49	0.00
Nitrogen, creatine.....	1.30	0.03	0.48	0.90
Nitrogen, purine.....	0.83	0.16	0.36	0.07
Nitrogen, undetermined meat bases.....	1.87	0.14	1.76	0.36

<sup>1</sup> *J. Soc. Chem. Ind.*, 1912, 31, 965.  
<sup>2</sup> *Conn. Agr. Expt. Stat. Rept.*, 1908, 606-672.  
<sup>3</sup> See Allen's *Comm. Org. Anal.*, 1913, Vol. VIII, 394.  
<sup>4</sup> c.c. *N*/10 KOH per gram of sample.

ANALYSES OF PROPRIETARY MEAT PREPARATIONS.

Brand	Water	Alcohol by weight	Organic matter	Ash	Petroleum ether extract	Chlorine	Phosphoric acid	Potash	Acidity, c.c. N/10 KOH per gram of material	Forms of nitrogen						Meat bases	Undeter- mined		
										Total	Insoluble	Coagulable	Ammonia	Pcp. by tannin-salt	Pcp. by phos- phate	Creatine	Creatine	Purines	Meat bases
.....	68.21	6.33	30.18	1.61	0.09	0.74	tr.	0.18	0.38	2.57	0.06	0.14	0.04	2.26	0.07	0.00	0.00	0.03	0.04
.....	68.18	0.00	0.46	1.36	0.09	0.14	0.42	0.02	0.98	1.30	0.00	0.05	0.00	0.85	0.34	0.00	0.00	0.00	0.16
.....	55.72	0.00	38.75	11.53	0.10	0.90	2.67	5.18	0.98	3.13	0.05	0.00	0.26	0.90	1.92	0.12	0.22	0.13	0.20
.....	53.81	0.00	29.02	17.17	0.02	4.75	3.06	4.42	4.74	3.35	0.12	0.41	0.19	0.85	1.08	0.20	0.28	0.16	1.23
.....	58.43	13.03	30.66	0.91	0.06	0.22	0.13	0.16	0.76	0.33	0.00	0.00	0.05	0.58	0.20	0.03	0.03	0.00	0.15
.....	51.17	13.23	17.98	0.83	0.02	tr.	tr.	0.02	0.20	0.10	0.00	0.02	0.12	0.07	tr.	0.00	tr.	0.00	0.00
.....	58.5	16.53	30.98	0.17	0.04	0.04	tr.	0.09	0.20	0.05	0.00	0.00	0.00	...	...	...	...	...	...
.....	51.82	14.19	37.04	1.14	0.00	0.24	0.18	0.33	7.02	1.12	0.00	0.00	0.00	0.72	0.36	0.03	0.00	0.03	0.24
.....	74.30	12.32	35.32	0.38	0.00	0.20	0.02	0.10	1.44	0.99	0.00	0.00	0.00	0.31	0.19	0.02	0.04	0.03	0.12
.....	74.33	8.00	35.75	0.72	0.30	0.19	0.04	0.14	0.29	1.59	0.30	0.00	0.13	0.64	0.28	0.00	0.00	0.00	0.28
.....	68.27	0.00	17.12	14.51	0.02	0.10	0.04	0.10	0.29	1.78	0.10	0.01	0.11	0.64	0.92	0.00	0.13	0.14	0.49
.....	43.15	0.00	41.14	18.71	0.19	2.34	2.83	2.27	6.42	4.09	0.10	0.07	0.20	1.23	1.97	0.30	0.13	0.31	1.05
.....	51.74	0.00	30.25	18.81	0.09	2.34	2.83	2.27	3.04	4.09	0.10	0.07	0.20	1.23	1.97	0.30	0.13	0.31	1.05
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Street also reports (*loc. cit.*) the analyses of certain proprietary meat preparations as shown on preceeding page.

Micko<sup>1</sup> has continued his extensive studies on meat extracts and bouillon cubes, and in the papers referred to discusses exhaustively the methods of analysis and the basis of interpretation of the results secured.

Einbeck<sup>2</sup> has isolated from meat extract. succinic acid and fumaric acid,<sup>3</sup> but could not establish the presence of malic acid. Krimberg and Izrailsky<sup>4</sup> isolated creatinine.

Salkowski<sup>5</sup> points out that zinc chloride and sodium carbonate precipitate purine bases, but from flesh extracts colloids which interfere with further isolation of the bases may also be precipitated. The colloids may be destroyed by heating the extract with dilute nitric acid before the zinc chloride treatment.

Smorodinzew<sup>6</sup> compared the yield of meat bases obtained by various sub-sulphate methods and found that treatment with a 10% mercuric solution in 5% sulphuric acid and precipitation of the filtrate, after removal of mercury, with phosphotungstic acid gave the best yields of purine bases and carnosine. The addition of sulphuric acid considerably reduced the yield of carnosine; the addition of lead salts likewise reduced the yield of carnosine and only slightly improved that of methylguanidine. Purine bases are not completely precipitated by phosphotungstic acid and their precipitation is apparently unaffected by lead salts or sulphuric acid.

Smorodinzew found ox flesh to contain 0.024% of purine, 0.265 of carnosine, 0.051 of methylguanidine and 0.029% of carnitine. He also found that extract of mutton contained twice the amount of purines and nearly twice the amount of carnitine found in beef extract, but only one-third the carnosine and one-half the methylguanidine. Mutton also contains more purines and carnitine and less carnosine and methylguanidine than horse flesh.

### Partition of Nitrogen in Meat Extracts.

Cook<sup>7</sup> has continued his studies on means of differentiating plant, yeast and meat extracts, using the methods previously employed together with the following method of Rippetoe for nitrogen precipitated by acid alcohol:

*Nitrogen Precipitated by Acid-Alcohol.*—Transfer 10 c.c. of an aqueous solution of the extract (= 1 grm.) to a 200 c.c. glass-stoppered measuring cylinder, add 1.2 c.c. of 12% hydrochloric acid, mix, add absolute alcohol to the mark, mix thoroughly and set aside for several hours at 20–25°. If necessary, make up to mark, filter and transfer 100 c.c. to a Kjeldahl flask, evaporate the alcohol on a water-bath and determine the nitrogen in the residue.

<sup>1</sup> *Zeit. Nahr. Genussm.*, 1913, 26, 321; 1914, 28, 489.

<sup>2</sup> *Zeit. physiol. Chem.*, 1913, 87, 145.

<sup>3</sup> Same journal, 1914, 90, 301.

<sup>4</sup> Same journal, 1913, 88, 324.

<sup>5</sup> *Biochem. Zeit.*, 1913, 55, 254.

<sup>6</sup> *Zeit. physiol. Chem.*, 1914, 92, 214, 221.

<sup>7</sup> *J. Amer. Chem. Soc.*, 1914, 36, 1551.

Cook found no creatine or creatinine and very little purine nitrogen in the plant extracts. The yeast extracts showed high purines and no creatine or creatinine. Plant and yeast extracts did not give the biuret reaction. All of the nitrogen of the plant extract was found in the filtrate after applying acid-alcohol, in the form chiefly of mono-amino acids and ammonia. About 25% of the nitrogen of the meat and yeast extracts is precipitated by acid-alcohol. The plant extracts yield a much larger percentage of ammoniacal nitrogen than the meat or yeast extracts.

PARTITION OF NITROGEN OF PLANT, YEAST, AND MEAT EXTRACTS.

	Percentage of total nitrogen								
	Total nitrogen	Ammonia nitrogen	Total creatinine nitrogen	Purine nitrogen	Nitrogen in phosphotungstic acid filtrate	Nitrogen in acid-alcohol filtrate	Nitrogen in tannin salt filtrate	Amino-nitrogen	
								Formol method	Van Slyke method
Meat extracts.	9.56	2.62	22.49	3.35	7.64	78.04	54.91	10.94	18.50
	9.65	2.49	22.59	3.52	6.84	78.45	55.85	10.94	18.23
	7.68	1.56	32.42	2.86	71.35	100.00	73.04	10.63	15.63
	9.65	.....	29.01	4.92	49.74	76.73	59.37	10.27 <sup>1</sup>	15.54
	7.49	.....	27.50	0.13	.....	89.19	64.21	9.53	17.89
Yeast extract.	5.35	2.43	0	11.22	49.96	72.15	56.07	17.64	32.71
Plant extracts.	5.23	7.46	0	0.42	85.85	100.00	94.46	36.71	65.77
	6.34	12.78	0	0.44	84.08	99.69	89.95	36.43	57.41
	6.33	.....	0	0.25	.....	100.00	83.41	30.64	45.18
	6.27	11.32	0	0.44	83.25	98.56	92.66	35.88	67.78
	6.47	6.03	0	.....	63.68	100.00	84.54	30.75	44.20
	6.08	12.98	0	0.46	84.04	99.67	92.76	35.85	61.18
	6.63	10.56	0	0.23	86.88	99.25	91.40	34.08	57.31

Bouillon Cubes.

Many analyses of these preparations have been reported and methods worked out for estimating the percentage of meat extract present.<sup>2</sup>

Cook<sup>4</sup> gives the following analyses of certain typical brands:

ANALYSES OF BOUILLON CUBES.

Brand	Solids, per cent	Organic matter, per cent.	Ether extract, per cent.	Ash, per cent.	Total chlorine as NaCl, per cent.	Total phosphoric acid, per cent.	Acidity (c.c. N/20 KOH per grm.)	Total nitrogen, per cent.	Nitrogen ppt. by acid-alcohol, per cent.	Total creatinine, per cent.
Behrend...	96.60	22.86	1.93	73.74	72.13	1.02	6.20	2.19	0.13	0.84
Oxo.....	95.06	25.31	3.10	69.75	65.00	1.51	6.50	2.97	0.86	1.07
Steero.....	96.05	28.41	1.20	67.64	62.15	1.83	9.15	3.62	0.76	1.67
Burnham..	96.87	41.94	1.00	54.93	52.90	0.58	6.10	2.11	0.05	0.88
Sunbeam..	95.73	45.23	1.44	50.50	49.26	0.54	7.30	2.36	0.02	0.92
Armour....	96.05	26.48	0.96	69.57	67.44	0.62	6.00	2.79	0.17	1.07
Morris.....	96.77	33.00	3.79	63.77	59.17	1.69	9.68	3.67	0.56	1.07
Standard..	95.81	21.76	4.19	74.05	72.22	0.48	5.01	2.09	0.07	0.50
Liggitt....	96.00	21.91	4.58	74.09	71.98	0.41	4.75	2.11	0.05	0.49
Knorr.....	95.44	26.24	4.57	69.20	65.00	1.55	7.40	3.20	0.91	1.38

<sup>1</sup> Not corrected for 15 % of the ammonia nitrogen.  
<sup>2</sup> Not corrected for ammonia nitrogen.  
<sup>3</sup> See Cook, *J. Amer. Chem. Soc.*, 1914, 36, 1551, and Micko, *Zeit. Nahr. Genussm.* 1913, 26, 321; 1914, 27, 489.  
<sup>4</sup> *J. Ind. Eng. Chem.*, 1913, 5, 989.

According to Serger,<sup>1</sup> if we place the creatinine content of meat extract at 6%, then bouillon cubes should contain the following amounts of creatinine for the respective amounts of meat extract used:

Meat extract used, per cent.	Creatinine contained, per cent.
25	1.5
20	1.2
15	0.9
10	0.6

Geret<sup>2</sup> found from results based on the analysis of 100 samples that the meat extract of bouillon cubes varied from 20 to 25% in the best cubes to none at all in the inferior grades, calculating the solids of high-grade meat extract at 80%. The cubes contain about 70% of water, fat and sodium chloride and 30% of any one or any combination of meat extract, plant extract and plant seasoning compound, the last named consisting of amino-acids derived from proteins by heating with acid until no biuret reaction is given, and then neutralising with soda.

Serger<sup>3</sup> claims that bouillon cubes should contain not more than 8% of water, 9 of fat, 65 of sodium chloride, and not less than 15% of meat extract. Good cubes contain between 92 and 98% of solids, 3.0 to 3.9 nitrogen, 0 to 5 sugar, 0.9 to 1.5 creatinine, 62 to 67 ash, 1.2 to 1.7 phosphoric acid, 18 to 25 protein and a ratio of *N/P* of 2.3 to 2.5.

Remy<sup>4</sup> analysing 10 high-grade samples found 12.3 to 17.8% of mineral matter (of which 11.3 to 16.2 was sodium chloride), 10.7 to 17 water and 2.1 to 10.6 fat. Inferior products containing as high as 60% of sodium chloride have been observed.

Kapeller and Gottfried<sup>5</sup> found 9 samples to range from 3.4 to 7.2% water, 4.4 to 10.9 fat, 9.8 to 24.8 albuminoids, 54.6 to 76.6 ash and 51.6 to 74.4 sodium chloride. The same chemists analysed 8 other samples as follows:<sup>6</sup>

Water	Albuminoids	Fat	Ash	Sodium chloride
6.5	13.4	6.7	65.9	63.3
3.3	14.6	8.2	56.3	54.9
4.4	14.1	6.2	69.1	66.2
3.4	10.1	5.7	77.2	74.5
3.8	9.6	8.3	70.4	69.4
3.3	6.6	10.5	73.1	72.5
5.6	6.0	7.0	70.6	69.1
1.1	0.5	2.9	83.7	83.0

Conti<sup>7</sup> analysed 3 samples as follows, the last consisting largely of gelatin and salt:

<sup>1</sup> *Konserven-Zeit.*, 48, 378.

<sup>2</sup> *Zeit. Nahr. Genussm.*, 1912, 24, 570.

<sup>3</sup> *Zeit. öffent. Chem.*, 1914, 20, 80, 101.

<sup>4</sup> *Pharm. Zentralh.*, 1913, 54, 1238.

<sup>5</sup> *Zeit. Nahr. Genussm.*, 1913, 26, 161.

<sup>6</sup> *Zeit. Nahr. Genussm.*, 1914, 28, 224.

<sup>7</sup> *Boll. chim. farm.*, 1913, 51, 183.

Water	Organic matter	Nitrogen	Fat	Ash	Sodium chloride	Phosphoric acid
6.5	17.0	2.48	4.2	71.9	65.0	1.06
7.0	22.0	2.49	7.1	63.0	60.0	0.40
22.0	51.5	7.64	.....	26.5	24.0	0.58

Krasser<sup>1</sup> found that Maggi's bouillon cubes during the years 1908-1911 ranged from 52.4 to 56.6% water, 21.9 to 27.2 organic matter, 20.0 to 25.7 albuminoids, 20.4 to 21.6 ash, 17.0 to 18.7 sodium chloride and 0.87 to 1.13 phosphoric acid.

Street<sup>2</sup> gives the following analyses of bouillon cubes and other condensed soups:

	Water	Fat	Ash	Protein	Carbo-hydrates	Nitrogen	Sodium chloride
Knorr's pea soup with bacon.....	9.6	9.0	15.0	21.4	45.0	3.42	12.5
Knorr's bean soup.....	11.0	6.2	16.0	19.3	47.5	3.09	12.8
Knorr's consommé.....	4.3	5.4	66.5	.....	.....	3.10	61.5
Steero bouillon cubes.....	6.6	1.7	65.2	.....	.....	3.89	59.5
Oxo bouillon cubes.....	4.8	3.6	67.5	.....	.....	3.28	62.7
Armour's beef extract and vegetable tablets.....	10.2	0.4	29.6	.....	.....	1.63	22.4
Mason's beef tea lozenges.....	10.8	0.1	9.7	.....	.....	<sup>3</sup> 13.04	2.2
Anker's bouillon capsules.....	8.6	0.1	47.1	.....	.....	5.54	38.4

Soups.

Street<sup>4</sup> analysed 6 brands of canned bouillon showing the following range of composition (over 99% of 1 brand consisting of water and salt):

	Max.	Min.	Ave.
Water.....	96.4	92.0	94.6
Ash.....	2.7	1.1	1.9
Ether extract.....	0.15	0.06	0.09
Protein (N X 6.25).....	2.09	0.49	1.39
Sodium chloride.....	2.48	0.93	1.63
Nitrogen.....	0.334	0.079	0.222
Undetermined.....	4.21	0.33	2.05

Congdon<sup>5</sup> has also investigated certain condensed soups. The amount of meat fibre in chicken soup ranged from 2.18 to 16.48%, the liquid portion from 6.01 to 83.88 and the other ingredients (chiefly boiled rice) from 13.94 to 90.32%. He showed that the average composition of 8 brands of "condensed" chicken soup was as follows:

Boiled rice.....	27.18
Meat extract.....	3.54
Meat fibre.....	8.10
Salt.....	2.05
Water.....	59.13

<sup>1</sup> *Zell. Nahr. Genussm.*, 1914, 27, 78.  
<sup>2</sup> *Conn. Agr. Expt. Stat. Rept.*, 1908, 660; 1911, 161; 1914, 238.  
<sup>3</sup> Contained much gelatin.  
<sup>4</sup> *Conn. Agr. Expt. Stat. Rept.*, 1910, 493.  
<sup>5</sup> *No. Dak. Food Dept. Spec. Bull.*, 1913, 2 (15), 246; 1914, 3 (5), 62



On the original basis these samples ranged from 81.4 to 94.1% water, 0.94 to 4.13 protein ( $N \times 6.25$ ), 0.07 to 1.96 water-soluble protein, 0.06 to 1.33 fat, 1.17 to 12.03 carbohydrates, 1.09 to 3.12 ash, and 0.92 to 2.83 salt. In some instances more beef fibre was present than chicken.

### Sausage.

**Water-content.**—Feder,<sup>1</sup> after analysing a large number of authentic samples, declares that the water should not exceed 60%. The ratio of water to fat-free organic matter is the most reliable index for added water, and should never exceed 4. This judgment has been confirmed by Schenck,<sup>2</sup> who found samples containing as much as 80% of water.

**Estimation of Benzoic Acid.**—Krüger<sup>3</sup> maintains that most of the previously proposed methods give unsatisfactory results in substances containing a large proportion of protein, difficulty being experienced in extracting the whole of the acid from such foods. He suggests the following method:

Mix 50 grm. of the finely divided meat with 45 c.c. of 70% sulphuric acid and submit to steam distillation. Collect 500 c.c. of the distillate, the flask being heated so as to maintain the volume of the contents as constant as possible. Filter the distillate, make slightly alkaline with sodium hydroxide and evaporate to a small volume. Heat the residual liquid on a water-bath and add potassium permanganate drop by drop until the pink colour remains for 5 minutes. Destroy the excess of permanganate with sodium sulphite, evaporate the mixture to 10 c.c., transfer to a separating funnel and acidify with sulphuric acid, rinsing the evaporating dish with sodium sulphite solution and dilute sulphuric acid and adding the washings to the funnel. Extract the acid solution, which should not exceed 20 c.c., with ether; wash the ethereal extract with water, allow the solvent to evaporate spontaneously in a weighed dish and weigh the residue after drying for 2 hours over soda-lime. The dried residue may be dissolved in alcohol and titrated with  $N/10$  sodium hydroxide. If the weight of benzoic acid is less than 30 mg., Polenske's sublimation method<sup>4</sup> should be used as a control.

### Composition of Meat Rations.

Gephart and Lusk<sup>5</sup> have made a valuable study of 242 ready-to-serve foods as dispensed by a well-known chain of restaurants in New York City. The various food portions were analysed, their calorific values determined, and a summary given of the cost of 2,500 calories in the various kinds of food purchased.

<sup>1</sup> *Chem. Zeit.*, 1914, 38, 709; *Zeit. Nahr. Genussm.*, 1913, 25, 577.

<sup>2</sup> *Zeit. Nahr. Genussm.*, 1915, 29, 145.

<sup>3</sup> *Zeit. Nahr. Genussm.*, 1913, 26, 12.

<sup>4</sup> *Analyst*, 1911, 36, 584.

<sup>5</sup> *Analysis and Cost of Ready-to-serve Foods*, Chicago, 1915.

## Eggs.

**Colouring Matter of Yolk.**—Barbieri<sup>1</sup> has shown this to be ovochromin, which decomposes at 270° and is a yellow, hygroscopic powder, soluble in its own weight of water, but insoluble in ordinary organic solvents. It is decolourised by hydrogen peroxide, but alkalis and concentrated acids have no action on it in the cold.

**Sugar Content.**—Morner<sup>2</sup> found that the sugar content, mainly glucose, of egg white varies from 0.3 to 0.5% in the common egg. In eggs of other species the lowest sugar was 0.12, the highest 0.32, and the average of 51 varieties 0.22%.<sup>3</sup>

**Estimation of Lecithin.**—Cohn<sup>4</sup> suggests the following method:

1 to 2 grm. of commercial lecithin preparations or 5 to 20 grm. of food containing lecithin are extracted for several hours with two successive portions of 100 c.c. of 96% alcohol, the first extraction at ordinary temperature, the second at the boiling temperature of alcohol, a reflux condenser being used. The residue is ground with sand, extracted once more with alcohol, and then boiled for 2 hours with about 100 c.c. of chloroform. When dealing with fatty substances it is advantageous to extract with chloroform immediately after the cold alcohol extraction. In certain cases the extraction with hot alcohol must be continued for 20 hours in order to extract all the phosphorus compounds. Evaporate the alcohol and chloroform extract, boil the residue for 2 hours with 100 c.c. of chloroform to separate the lecithin from glyceryl-phosphoric acid and free phosphoric acid; filter the solution and evaporate. The amount of phosphorus in the residue is estimated by oxidising with nitric and sulphuric acids, or igniting it with the addition of magnesium oxide, or a mixture of sodium carbonate and potassium nitrate, precipitating the resulting phosphoric acid with molybdic acid solution and continuing in the usual way.

**Estimation of Salicylic Acid in Preserved Eggs.**—Froidevaux<sup>5</sup> has pointed out that salicylic acid cannot be determined in preserved eggs by the usual procedure. If a mineral acid is used to liberate salicylic acid, an unfilterable magma results. If the magma be treated with ether to extract the salicylic acid, emulsions form, and fats, lipochromes, lecithin, etc., pass into the solvent. He proceeds as follows:

To 25 grm. of powder or 30 grm. of liquid egg contained in a 500 c.c. porcelain dish 250 c.c. of water are added, the mixture stirred, 125 c.c. of 8% sodium hydroxide solution added and the mixture warmed for 45 minutes on the water-bath. The resultant gelatinous mass is broken up with a glass rod and the particles washed with water by decantation and on the filter. The filtrate is acidified with hydrochloric acid and 20 c.c. of sodium phospho-

<sup>1</sup> *Compt. rend.*, 1912, 154, 1726.

<sup>2</sup> *Zeit. physiol. Chem.*, 1912, 80, 430.

<sup>3</sup> See also Bierry, Hazard and Ranc, *Compt. rend. soc. biol.*, 1914, 73, 93.

<sup>4</sup> *Zeit. Offent. Chem.*, 1913, 19, 54.

<sup>5</sup> *J. pharm. chim.*, 1915, 10, 18.

molybdate solution added to precipitate the protein. The filtrate from this is extracted with ether in the usual way. The method is sensitive to 0.0023 grm. in 100 grm. of material.

**Distinguishing between the Whites of Hen and Duck Eggs.**—Waterman<sup>1</sup> prepared sera by injecting the white of hen eggs and duck eggs respectively into rabbits and drawing off the blood a week after the last injection. These sera were standardised by adding to 0.1 c.c. of the serum 1 c.c. of standard solutions of white of hen and of duck eggs, respectively, ranging in strength from  $\frac{1}{1,000}$  to  $\frac{1}{80,000}$ . A precipitate is formed at the junction of the liquids. The greatest dilution at which this precipitate is formed is taken as the titre of the serum. The whites of the two kinds of eggs should react only with their respective sera. The sample to be tested is made up to various concentrations and treated as above. When the sample is a mixture it will react with both sera. One analysis showed 60% of white of duck eggs and 40% of hen egg white.

**Estimation of Albumin.**—Labbé and Maguiso<sup>2</sup> have proposed a volumetric method in which the egg albumin is precipitated by the citropicric acid reagent prepared according to Esbach.

### Fish.

**Composition.**—Williams<sup>3</sup> gives very complete analyses of 25 varieties of English fish.

**Anchovy Butter.**—Behre and Frerichs<sup>4</sup> claim that true anchovy butter is characterised by a lower fat content and lower iodine number and refraction of the extracted fat than herring butter, or a mixture of the two. In general, anchovy butter containing less than 10% of fat contains no foreign fish; that containing about 15% of fat must be regarded as suspicious if the iodine number exceeds 60 and the refraction 50. The addition of foreign fish cannot be detected in mixtures containing equal parts of fish and butter.

**Nitrogen of Fish Muscle.**—Wilson<sup>5</sup> has studied the partition of the nitrogen in extracts of the muscles of the lamprey, limulus, squid, clam, scallop and periwinkle. Betaine was isolated from the scallop, periwinkle and lamprey; creatine from the lamprey.

Okuda<sup>6</sup> obtained the following results in grams per 100 grm. of dry substance:

<sup>1</sup> *Chem. Weekblad.*, 1913, 11, 120.

<sup>2</sup> *Compt. rend.*, 1913, 156, 1415.

<sup>3</sup> *Chem. News*, 1911, 104, 271.

<sup>4</sup> *Zeit. Nahr. Genussm.*, 1912, 24, 676.

<sup>5</sup> *Jour. Biol. Chem.*, 1914, 17, 385; 1914, 18, 17.

<sup>6</sup> *8th Int. Cong. App. Chem.*, 1912, 18, 275.

	Creatine	Creatinine
Bonito.....	2.01	0.48
Tunny fish.....	1.80	0.23
Salmon.....	1.53	0.18
Snapper.....	3.33	0.31
Carp.....	2.02	0.37
Shark.....	3.24	0.66
Lobster, crab, clam and cuttlefish.....	trace	trace

Yoshimura and Kanai<sup>1</sup> found dried codfish to yield per kilogram 1.4 grm. of creatinine, 0.44 betaine hydrochloride, 0.70 methylguanidine picrate, 13 taurine, 0.50 alanine, traces of glutamic acid, and no creatine or choline.

**Glycogen in Fish.**—Schöndorff and Wachholder<sup>2</sup> found the glycogen content of fish muscle to range from none to 0.68%.

**Caviare.**—König and Groszfeld<sup>3</sup> found fish roe to contain xanthine, hypoxanthine, creatinine, taurine, *L*-tyrosine, glycocoll, thymine, proteins soluble and insoluble in water, and fat. The proteins are rich in sulphur and phosphorus and do not yield protamines. The fat is characterised by a high lecithin content (up to 59%) and also contains from 3.9 to 14% of cholesterol.<sup>4</sup>

Helen Chernoruzkii<sup>5</sup> found 1.2 grm. of nucleic acid in 100 grm. of freshly dried and alcohol-ether extracted herring eggs.

Kodama<sup>6</sup> has shown that by means of the precipitin, anaphylaxis (active and passive) and complement-binding reactions, caviare can be differentiated from other fish spawn, such as carp, red eye, bream, tench, salmon, herring and trout. By means of the precipitin reaction the fish-roe protein can be clearly differentiated from the fish protein of the same animal.

Dinslage<sup>7</sup> found a sample of caviare preserved with urotropin (hexamethylenetetramine), which he identified by means of Rimini's method as modified by Arnold and Mentzel.<sup>8</sup>

<sup>1</sup> *Zeit. physiol. Chem.*, 1913, 88, 346.

<sup>2</sup> *Pflüger's Arch. Physiol.*, 1914, 157, 147.

<sup>3</sup> *Biochem. Zeit.* 1913, 54, 338, 351.

<sup>4</sup> For detailed analyses see above paper and also *Zeit. Nahr. Genussm.*, 1914, 27, 502.

<sup>5</sup> *Zeit. physiol. Chem.*, 1912, 80, 194.

<sup>6</sup> *Arch. Hyg.*, 1913, 78, 247.

<sup>7</sup> *Zeit. Nahr. Genussm.*, 1913, 26, 200.

<sup>8</sup> *Zeit. Nahr. Genussm.*, 1902, 5, 353.

# FIBROIDS.

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By W. P. DREAPER, F. I. C.

## ESTIMATION OF SMALL QUANTITIES OF WOOL IN COTTON MATERIALS.

This is a matter of some importance under modern conditions. The wool is separated by P. Heerman<sup>1</sup> in the following manner: Sulphuric acid (80%) dissolves cotton completely in 2–3 hours, whilst wool only loses 1.5% of its weight in the same time. In practice the sample (5–10 grm.) is thoroughly extracted with ether and then with 96% alcohol, and the fibre is then treated with ten to twenty times its weight of the acid. After standing 6 hours the cotton has completely dissolved. The liquid is diluted with water (cold) and any wool present remains undissolved; it may be dried at 105° after a thorough washing with water and weighed (an allowance of 17% being made for moisture).

<sup>1</sup> *Chem. Zeit.*, 1913, 1257.



## APPENDIX

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**Sugars.**—For the use of enzymes and special yeasts in carbohydrate analysis reference should be made to a paper by W. A. Davis in the *J. Soc. Chem. Ind.*, 1916, 35, 201. This deals with the question of the estimation of saccharose, raffinose, maltose and starch. For estimating raffinose, the material proposed by Hudson & Harding (*J. Amer. Chem. Soc.*, 1915, 37, 2193), using autolysed top and bottom yeasts, is at the present moment probably the most accurate and most convenient. Regarding the supposed precipitation of reducing sugars by basic lead acetate see Davis (*J. Agric. Science*, 1916, 7, 255).

For the estimation of small quantities of reducing sugars in presence of large quantities of saccharose see Maquenne (*Compt. rend.*, 1915, 161, 617; 1916, 162, 145, 207 and 277). For details of the estimation of sugars in plant material and a discussion of the question of the formation and translocation of sugars in the tissues see Davis (*J. Agric. Sci.*, 1916, 255, 328, 352); for the question of the presence of maltose in leaves and in germinated barley and its influence on the measurement of amylolytic power, see Davis (*Biochemical J.*, 1916, 31). W. A. D.

**Butter.**—It has been the experience of several observers, besides the writers, that + values for the "difference figure" have been obtained in the case of several butters of undoubted purity during the later months of last year (1915). These butters are particularly of Irish origin and the probable reason is the difficulty of obtaining proper feeding stuffs arising out of war conditions. Butters from sources not so affected have not shown any departure from the normal. C. REVIS.

**Arginine.**—Clemanti (*Atti. R. Accad. Lincei*, 1914, 23, ii, 517 and 611) has shown that arginase, an enzyme present in liver extracts, converts arginine quantitatively into urea and ornithine. It is probable that this reaction will afford a convenient means of estimating arginine, either following the change by measuring the new amino-group produced by a formalin titration method (Clementi) or by determining the urea produced by the urease method (Plimmer). For a discussion of the ordinary method of estimating arginine see Plimmer (*Biochemical J.*, 1916). W. A. D.

**Meat Extracts.**—For the methods adopted in the estimation of nitrogenous constituents of extracts derived from albuminous substances such as meat extracts with special reference to the interpretation of the results see the report of the discussion on this subject in the *Analyst*, July, 1915.





# INDEX

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- ACETANILIDE** and phenacetin, estimation of in admixture, 472  
**Acetic acid**, 90  
**Aceto-acetic acid**, estimation of, 577  
**Acetone**, estimation of, 576  
**Acetyl-salicylic acid**, 306  
**Acids, animal**, 569  
**Aconite alkaloids**, 487  
 —assay of, 488  
 —toxicological detection of, 489  
**Aconitine**, constitution of, 487  
**Aconitum napellus**, alkaloids of, 487  
 —*vulparia*, alkaloids of, 488  
**Adenine**, 568  
**African copaiba oil**, 315  
 —*elemi*, 318  
*d*-Alanine and *d*-Valine, separation of, 562  
**Albuminoids**, 604  
**Alcohol, ethyl**, 4  
 —methyl, 1  
**Alcoholic derivatives, neutral**, 18  
**Alcohols**, 1  
**Aliphatic acids**, 90  
**Alizarin oil**, 145  
**Alkaloids, aconite**, 487  
 —*areca*, 480  
 —*broom*, 541  
 —*calabar*, 537  
 —*cinchona*, 514  
 —*colchicum*, 534  
 —*conium*, 481  
 —*ergot*, 537  
 —*ipecacuanha*, 541  
 —constitution, of 544  
 —*jaborandi*, 537  
 —*lupine*, 481  
 —*opium*, 496, 504  
 —*solanine*, 540  
 —*strychnos*, 510  
 —*vegetable*, 477, 534  
 —formation of, 477  
 —function of, 478  
 —precipitants for, 479  
 —properties of, 478  
 —volatile, 480  
**Almond oil**, 129, 349  
**Aloes**, detection of, 549  
**American wormseed oil**, 382  
**Amines**, 469  
**Amino-acids**, 575  
 —in meat products, 609  
 —nitrogen, estimation of by Sørensen's method, 561  
 —picrolonates of, 562  
 —separation of, 561  
**Ammonia** and trimethylamine, estimation of, 469  
**Ammoniacum**, 315  
**Ammonium benzoate**, 285  
**Amyrol**, 343  
**Anchovy butter**, 621  
**Andropogon oils**, 345  
**Angelica oil**, 350  
**Anhydro-pilosine**, 538  
**Aniseed oil**, 351  
**Anthranoyl-lycoctonine**, 488  
**Antipyrine**, estimation of, 470  
 —tests for, 470  
**Apomorphine**, 499  
**Aporeine**, 501  
**Apricot kernel oil**, 129  
**Arabinose**, reducing power of, 62  
**Arachis oil**, 126  
**Areca alkaloids**, 480  
**Arecolidine**, 480  
**Arginine**, 625  
**Argols**, London method for, 100  
**Aristoquinine**, 519  
**Artemisia bitters**, 550  
**Asafoetida**, 316  
**Asparox**, 614  
**Aspartic acid**, estimation of in protein hydrolysis, 592  
**Asphalt**, 240  
 —analysis of, 240  
 —drip point, 243  
 —ductility of, 242  
 —float test for, 243  
 —hard, estimation of, in mineral oils, 249  
 —melting point of, 242  
 —natural, estimation of, 245  
 —and petroleum, separation of, 245  
 —products, detection of, in tars, 278  
**Asphaltum**, estimation of paraffin in, 244  
 —natural, detection of, in coal tar residues, 277  
**Atractylol**, 343  
**Atropine**, detection of, 491  
 —estimation of, 493  
**Balsam, Peruvian**, 295  
**Balsams, aromatic**, 294  
 —cinnamic, 295  
**Barley**, analysis of, 6  
**Bases, animal**, 560  
 —ninhydrin tests for, 560  
 —Van Slyke apparatus for, 560

- Bassia tallow, 146  
 Bay oil, 352  
 Beer, 11  
 Beet molasses, 47  
 Belladonna, assay of, 492  
 Benzaldehyde, assay of, 288  
 ———estimation of, 286  
 Benzoic acid, commercial, detection of  
 ———halogens in, 279  
 ———detection of, 279  
 ———estimation of, 283  
 ———in urine, 574  
 ———aldehyde, 286  
 Benzols, commercial, testing, 259  
 Berberine, 521  
 ———detection of, 521  
 ———estimation of, 521  
 Bergamot oil, 352  
 Betaine hydrochloride, 563  
 Betulol, 343  
 Bile acids, 578  
 ———pigments, 579  
 ———Bonanno's test for, 580  
 ———Salkowski-Schipper test for, 580  
 Bisabolene, 325  
 Bismuth salicylate, 304  
 Bitumens, 240  
 ———estimation of oxygen in, 250  
 Blood, estimation of aceto-acetic acid in,  
 ———577  
 ———acetone in, 576  
 ———uric acid in, 572  
 Bonanno's test for bile pigments, 580  
 Borneo tallow, 149  
 Borneol, 342  
 Bouillon cubes, analyses of, 616  
 Bovinine, 614  
 Bovox, 614  
 Bovril, 614  
 Brucine, detection of, in strychnine, 510  
 Buchu oil, 353  
 Butter, difference figures for, 625  
 ———estimation of curd in, 162  
 ———fat in, 158  
 ———salt in, 162  
 ———water in, 155  
 ———fat, 152  
  
 Cadinene, 325  
 Caffeine, estimation of, 526  
 ———sodium salicylate, assay of, 526  
 ———toxicity of, 528  
 Caffeol, 531  
 Calabar alkaloids, 536  
 Calamus oil, 353  
 Calcium cyanamide, estimation of, 590  
 Calculi, urinary, 580  
 Camphor, detection of, in shiu oil, 367  
 ———oil, 353  
 Canada Balsam, 312  
 Cananga oils, 382  
 Candle nut oil, 138  
 Cane molasses, 46  
 Caramel, analysis of, 7  
 ———in vinegar, 96  
  
 Carbohydrates, estimation of, in plant  
 ———extracts, 64  
 Carbolic acid, crude, estimation of phe-  
 ———nol in, 270  
 Carbonyl ferrocyanides, 588  
 Cardamon oil, 354  
 Caryophyllene, 325  
 Casein, ash free, preparation of, 595  
 ———estimation of, 596  
 ———molecular weight and valency of, 596  
 Caseinates, 595  
 Cassia oil, 293, 354  
 Caviare, 622  
 Cedrene, 325  
 Cedrol, 343  
 Celery oil, 356  
 Cellulose, 77  
 Cephaeline, 543  
 ———salts of, 543  
 Cereals, estimation of starch in, 76  
 Ceresin and paraffin, analysis of mix-  
 ———tures of, 257  
 Champaca oil, 357  
 Cheese, analysis of, 600  
 Chestnut-oak bark, 396  
 Chinese wood oil, 140  
 Chloroform, 18  
 Chlorogenic acid, detection of, 531  
 Cholesterol, estimation of, in animal  
 ———tissues, 223  
 Chondroitin-sulphuric acid, 574  
 Chrome leather, analysis of, 414  
 Cibil's fluid extract, 614  
 Cider vinegar, 94  
 Cinchona alkaloids, constitution of, 515  
 ———estimation of, 514  
 ———test for, 515  
 ———ledgeriana seeds, 514  
 Cinchonine hydrochloride, impurity in,  
 ———520  
 Cineol, 343  
 Cinnamic acid, detection of, 291  
 ———estimation of, 292  
 ———balsams, 295  
 Cinnamon bark oil, 356  
 ———leaf oil, 356  
 ———oil, 292, 354  
 Citral, 344  
 ———estimation of, 337  
 Citrate of lime, analysis of, 109  
 Citric acid, estimation of, 111  
 Citronella oils, 345  
 Citronellal, 344  
 Citronellol, 341  
 Clove oil, 358  
 Clovene, 325  
 Coal tar residues, detection of natural  
 ———asphaltum and petroleum pitch  
 ———in, 277  
 Cocaine, separation and identification of,  
 ———494  
 Codeine, 500  
 Coffee, 530  
 ———estimation of caffeine in, 526  
 ———extracts, 532

- Coffee**, moisture in, 530  
 —substitutes, 531  
 —toxicity of, 531  
**Colchicine**, 534  
 —bromo derivatives of, 534  
 —derivatives, physiological action of, 534  
**Colchicum** alkaloids, 534  
**Colden's** liquid beef No. 2, 614  
**Colouring** materials, analysis of, 419  
 —fastness of, 419  
 —natural, 427  
**Colours**, fastness of, 419  
**Condensed** milk, estimation of saccharose in, 56  
**Coniine** methonitrite, 481  
**Coniinium** nitrite, 481  
**Conium**, assay of, 481  
**Copaiba**, 313  
 —African, detection of, 313  
 —oil, 314, 315  
**Copal**, 310  
**Cotton** materials, estimation of small quantities of wool in, 623  
 —seed oil, 135  
**Coumarin**, 293  
**Cream**, aldehyde figure for, 599  
 —regulations for, 597  
 —of tartar, 103  
**Creatine**, estimation of, 567, 610  
 —preparation of, 565  
**Creatinine**, estimation of, 566, 610  
 —preparation of, 565  
**Creosote**, antiseptic properties of, 276  
 —coke test for, 276  
 —oils, testing of, 275  
**m-Cresol**, estimation of, 273  
 —by Raschig's method, 273  
**Cresols**, estimation of, 272  
**Croton** oil, 146  
**Cubeb** camphol, 343  
**Cubebs**, oil of, 358  
**Cuprea** bark, 514  
**Cutch**, 395  
**Cyanamide**, 589  
**Cyanides**, detection of, 585  
 —double, 587  
 —estimation of, 586  
**Cyanogen** and iron, compounds of, 587  
 —spectroscopic detection of, 585  
**Cycloparaffins**, 236  
**Cypress** leaf oil, 359  
**Cystine** and tyrosine, separation of, 563  
**Cytisine**, 534  
 —assay of, 536  
**Cytisoline**, 535  
  
**Dammar** resin, 310  
**Digitalis**, 546  
**Digitonin**, 546  
**Digitoxin** and gitalin, separation of, 547  
**Dionin**, 500  
**Dipeptides** in meat products, 609  
**Dragon's** blood, 311  
**Dyes**, fastness of, 419  
  
**Easton's** syrup, alkaloids in, 518  
**Eggs**, 620  
**Elemi**, 318  
**Emetine**, 542  
 —salts of, 543  
**Enzymes**, 591  
**Ergot** alkaloids, 537  
**Eserine**, 536  
**Eseroline**, 536  
**Essential** oils, 324, 345  
**Ether**, 18  
**Ethoxylupanine** dihydrobromide, 482  
 —dihydroiodide, 482  
 —thiocyanate, 482  
**Ethyl** alcohol, 4  
 —chloride, 18  
 —citrate, 331  
**Eucalyptus** oil, 359  
**Eudesmol**, 343  
**Euquinine**, 519  
  
**Farnesol**, 342, 343  
**Fat**, extraction of, 117  
**Fenchene**, 325  
**Fenchyl** alcohol, 343  
**Pennel** oil, 360  
**Ferrocyanides**, estimation of, 588  
**Fibres**, dyed, examination of, 419  
**Fish**, 621  
**Flour**, 593  
**Fluxes**, 243  
**Foods** canned, estimation of tin in, 612  
 —colouring matters in, 449  
 —regulations for preservatives in, 597  
**Formic** acid, 97  
**Formolite**, 235, 238  
**Fruit** juices, estimation of citric acid in, 113  
  
**Galbanum**, 318  
**Gaultheria**, natural, 305  
**Gelatin**, detection, of, 605  
**Genisteine**, 483  
 —salts of, 483  
**Geraniol**, 341  
**Geranium** oil, 361  
**Ghee**, 175  
**Ginger** oil, 362  
**Ginger-grass** oil, 347  
**Gitalin** and digitoxin, separation of, 547  
**Gitonin**, 547  
**Glucosides**, 545  
 —cyanogenetic, 545  
 —synthetic, 545  
**Glue**, detection of, 605  
**Glutamic** acid, estimation of in protein hydrolysis, 592  
**Glycerin**, crude, specifications for, 219  
 —pure, 220  
**Glycerinum**, 220  
**Glycerol**, 211  
 —crude, analysis of, 211  
 —estimation of, by the acetin process, 214  
 —dichromate process, 217

- Glycerol, estimation of, in fats, 222  
     — in wines, 221, 222  
 Glycerol-acryl, 221  
 Glyceryl acetate, 332  
 Glycogen, 607  
 Glycuronic acid, 575  
 Gold cyanide, 585  
 Guaiacum, 311  
 Guaiol, 343  
 Gum benzoin, 294  
 Gurjun balsam, detection of, 315  
  
 Heerabolene, 325  
 Hemp seed oil, 139  
 Heroin, 499  
 Hides, East Indian, analysis of, 414  
 Hippuric acid, 569  
 Homogentisic acid, 569  
 Hop oil, 362  
 Hops, 550  
     — commercial analysis of, 554  
     — estimation of antiseptic power of, 557  
     — arsenic in, 559  
     — bitterness of, 558  
 Hydrastine, detection of, 522  
     — estimation of, 523  
 Hydrastinine, 524  
 Hydrastis, fluid extract of, 523  
     — rhizome, assay of, 523  
 Hydrazine, estimation of, 470  
     — nitrate, 469  
 Hydrocarbons, 229  
     — aromatic, 234  
     — estimation of in admixture with  
         paraffins, 263  
     — unsaturated hydrocarbons  
         in, 264  
     — cyclic, 259  
     — separation of, by chemical methods,  
         232  
     — physical methods, 229  
 Hydrochloric acid in gastric juice, 580  
 Hydrocyanic acid, detection of, 585  
     — estimation of, 586  
 Hydroferricyanic acid, estimation of, 588  
 Hydro-ipecamine, 542  
 Hydroquinine, 519  
     — sulphate, preparation of, 519  
 $\beta$ -Hydroxybutyric acid, 578  
 Hyoscine, 490  
 psuedo-Hyoscyamine, 490  
  
 India-rubber, 320  
     — estimation of, 321  
     — latex, analyses of, 320  
 Indigo, analysis of, 427  
     — in presence of starch, 446  
 Indigo-dyed materials, analysis of, 436  
 Indole and pyrrole, distinction between,  
     476  
 Inks, printing, 456  
     — analysis of, 457  
     — black, 460  
     — blue, 463  
     — composition of, 456  
  
 Inks, printing, green, 464  
     — manufacture of, 457  
     — permanence to light of, 466  
     — red, 463  
     — special tests for, 467  
     — writing, estimation of tannin in, 468  
 Inositol, detection of, in meat products,  
     608  
 Invert sugar, analysis of, 7-9  
     — estimation of, 39  
 Ipecacuanha alkaloids, 541  
     — constitution of, 544  
 Ipecamine, 542  
 Iron and cyanogen, compounds of, 587  
  
 Jaborandi alkaloids, 537  
 Japanese wood oil, 144  
 Juniper berry oil, 363  
  
 Kapok oil, 135  
 Kola, 532  
 Kynurenic acid, 569 .  
  
 Lactic acid, 582  
     — estimation of, 582  
     — in meat products, 608  
 Lactose, estimation of, 57  
 Lalaloe oil, 366  
 Lard, 178  
 Lavender oils, 363  
 Leather, American, analysis of, 415  
     — analysis of, 411  
 Ledum-camphor, 343  
 Lemon-grass oil, 346  
 Lemon juice, analysis of, 110  
     — oil, 365  
 Lime juice, analysis of, 110  
     — oil, 365  
 Linalol, 341  
 Linalyl acetate, 331  
 Linolenic acid, 184  
 Linosyn, 189  
 Linseed cake, 182  
     — oil, 180  
 Lobeline, 481  
 London method for the analysis of tar-  
     tars, 100  
 Lubanol, 294  
*d*-Lupanine, 482  
     — dihydrobromide, 482  
 Lupanine, inactive, 482  
 Lupine alkaloids, 481  
 Lycaconitine, 488  
 Lycoctonic acid, 488  
 Lycoctonine, 488  
  
 Maggis bouillon, 614  
 Malic acid, estimation of, 98  
 Mallet bark, 396  
 Malt, 5  
 Maltose, estimation of, 53  
 Malts, analysis of, 6  
 Mangrove, 395  
 Manila elemi, 318  
 Margarine, 166

- Margarine**, analysis of, 174  
**Mason's essence of beef**, 614  
**Meat**, 607  
     —decomposition of, 612  
     —frozen, 613  
     —extracts, 613  
     —nitrogenous constituents of, 625  
     —partition of nitrogen in, 615  
     —products, 607  
     —estimation of ammonia in, 612  
     —phosphorus compounds in, 611  
     —rations, composition of, 619  
**Mechanical pulp**, 86  
**Menthol**, 343  
**Methyl alcohol**, 1  
     —salicylate, 305  
**Methylcytisine**, 536  
**N-Methylcytisine**, 535  
**Milk condensed**, estimation of sugars in, 597  
     —dried, analysis of, 600  
     —products, 597  
     —proteins of, 595  
**Morphine**, detection of, 497  
     —estimation of, 497, 506  
     —in opium, 504  
     —salts of, 497  
     —toxicology of, 508  
**Morphine-narcotine meconate**, 503  
**Mosquera beef meal**, 614  
**Mulford's predigested beef**, 614  
**Murdock's liquid food**, 614  
**Muscle extractives**, 607  
     —nitrogenous, 609  
**Mustard oil**, 134  
**Myoctonine**, 488  
**Myrabolans**, 395  
**Myrcene**, 324  
**Myrrh**, 318  
     —oil of, 319  
  
**Naphtha**, heavy, analysis of, 249  
**Naphthalene**, estimation of, 236  
     —in coal gas, 266  
     —in spent oxide, 268  
**Naphthenes**, 236  
 $\beta$ -**Naphthol**, estimation of, 269  
     —Pharmacopœia requirements for, 269  
**Naphthols**, reaction of, with tetravalent titanium, 272  
**Narcophine**, 503  
**Narcotine**, 501  
**Nerol**, 341  
**Nerolidol**, 342, 343  
**Neutraline**, 120  
**Nicotine**, estimation of, 485  
**Ninhydrin test for animal bases**, 560  
**Nitrogen**, colloidal, of urine, 575  
**Nitrosoconiine**, 481  
**Non-glucosidal bitter principals**, 549  
**Noratropine**, 490, 491  
**Norhyoscyamine**, 490, 491  
**Nux vomica**, 510  
     —assay of, 512  
     —oil of, 510  
  
**Oak bark**, 397  
**Ocimene**, 324  
**Oil of cassia**, 293, 354  
     —cinnamon, 292, 354  
     —cubebs, 358  
     —myrrh, 319  
     —rue, 369  
**Oils**, drip testing of, 261  
     —essential, 324, 345  
     —alcohols in, 328  
     —aldehydes in, 336  
     —citral in, 337  
     —esters in, 330  
     —free acids in, 325  
     —phenols in, 327  
     —refractive indices of, 339  
     —gas, for railways, specifications for, 255  
     —hardened, 122  
     —marine animal, 123  
     —lubricating, tests for, 251  
     —mineral, estimation of asphalt in, 246  
         —hard asphalt in, 249  
         —paraffin in, 257  
         —sulphur in, 247  
     —lubricating, evaporation test for, 256  
     —specific gravity of, 247  
     —oxidation of, 118  
     —petroleum, carbon test for, 250  
     —transformer, 256  
     —wood-preserving, antiseptic tests for, 276  
         —phenols in, 271  
**Olefines**, 233  
     —estimation of, 233  
**Olive oil**, 131  
     —saponified, 132  
**Opiopon**, 502  
**Opium**, adulteration of, 504  
     —alkaloids, 496, 504  
     —bases, 496  
     —estimation of morphine in, 504, 507  
     —normal, 506  
     —toxicology of, 508  
**Opon**, 502  
**Orange oil**, 368  
**Otto of rose**, 373  
**Oxalic acid**, 97  
     —in urine, 574  
  
**Palmarosa oil**, 347  
**Panopepton**, 614  
**Pantopon**, 502  
**Paper**, 80  
**Paracasein**, molecular weight and valency of, 596  
**Paracaseinates**, 595  
**Paraffin and ceresin**, analysis of mixtures of, 257  
**Paraffins**, 238  
**Patchouli-camphor**, 343  
**Peach-kernel oil**, 130  
**Pentoses**, 62  
**Peppermint oil**, 370

- Pepto-mangan "Gude," 614  
 Peptonoids, liquid, 614  
 Peruvian balsam, 295  
 Petitgrain oil, 369  
 Petroleum, crude, water in, 249  
 —detection of, in tars, 278  
 —estimation of sulphur in, 247  
 —pitch, detection of, in coal tar residues, 277  
 Phellandrene, 324  
 Phenacetin and acetanilide, estimation of, in admixture, 472  
 Phenol, bromination of, 271  
 —estimation of, 270  
 Phenolcarboxylic acids, reaction of, with tetravalent titanium, 272  
 Phenols, 270  
 —reaction of, with tetravalent titanium, 272  
 Phenol-*p*-sulphonic acid, estimation of, 279  
 Phenyl salicylate, 305  
 Phosphorus in meat and eggs, 611  
 Physostigmine, 536, 537  
 Physostigmol, 537  
 Phytosterolins, 545  
 Pilosine, 537  
 —constitution of, 539  
 —physiological action of, 540  
 —salts of, 538  
 Pilosinine, 538  
 Pine needle oil, 372  
 —nut oil, 139  
 Pinene, 324  
 Pitch, petroleum, estimation of asphalt in, 246  
 Piturine, 482  
 Plant extracts, estimation of carbohydrates in, 64  
 Polymethylenes, 236  
 Poppy seed oil, 139  
 Protein hydrolysis, estimation of aspartic and glutamic acids in, 592  
 Proteins, vegetable, 593  
 Psychotrine, 544  
 —salts of, 544  
 Purine bases, 525  
 Purines in muscle extracts, 610  
 Pyramidone, tests for, 471  
 Pyridine, detection of, 475  
 —estimation of, 475  
 Pyroligneous acid, 96  
 Pyrrole and indole, distinction between, 476  
  
 Quebracho, 398  
 Quinine, 516  
 —detection of, 516  
 —dihydrochloride, 517  
 —estimation of, 516  
 —formate, 518  
 —glycerophosphate, 518  
 —hydrochloride, 517  
 —salts, of, 517  
 —and strychnine, separation of, 518  
  
 Quinine, sulphate, 517  
  
 Raffinose, estimation of, 52  
 Rape oil, detection of, in olive oil, 131  
 Resins, 310  
 Rideal-Walker phenol control, 277  
 Roofing papers, 244  
 Rose oil, 373  
 Rosemary oil, 374  
 Rue, oil of, 369  
  
 Saccharin, commercial, 288  
 —detection of, 288  
 —estimation of, 290  
 Saccharose, 43  
 —estimation of, in brewing, 9  
 Safflower oil, 139  
 Salicylates, estimation of, 304  
 Salicylic acid, 299  
 —estimation of, 301  
 —esters, 305  
 Salkowski-Schipper's test for bile pigments, 580  
 Salol, 305  
 Santalene, 325  
 Santalol, 343  
 Santalwood oil, 375  
 Santonin, estimation of, in wormseed, 550  
 Saponification, 118  
 Sarsaparilla, 548  
 Sarsapic acid, 548  
 Sarsasaponin, 548  
 Sausage, 619  
 Selinene, 325  
 Sesame oil, 136  
 Sesquiterpenes, 325  
 Shea butter, 147  
 —nut oil, 148  
 Shellac, 311  
 Shiu oil, 367  
 Sinuox, 614  
 Sitosterol, 548  
 Sitosterol-*d*-glucoside, 548  
 Soap, 204  
 —powders, 209  
 —scouring, 209  
 Soaps, cresol, 208  
 Sodio-theobromine salicylate, 305  
 Sodium benzoate, 285  
 —cyanide, 585  
 —salicylate, 304  
 —zinc cyanide, 587  
 Soja-bean oil, 137  
 Solangustidine, 541  
 —salts of, 541  
 Solangustine, 540, 546  
 Solanine alkaloids, 540  
 Somatose, 614  
 Soups, analyses of, 618  
 Sparteine, salts of, 483, 541  
 Spearmint oil, 372  
 Starch, estimation of, 70  
 —sugars, estimation of, in brewing, 10  
 Stigmasterol, 548  
 Storax, liquid, 297



- Strophanthin**, 547  
**Strychnine**, detection of, in brucine, 510  
 —and quinine, separation of, 518  
**Strychnos alkaloids**, 510  
**Styrax liquidus**, 298  
 —*præparatus*, 298  
 —*purificatus*, 297  
**Succinic acid**, 97  
**Sugar analysis**, 49  
**Sugars**, 19, 625  
 —estimation of, 22  
 —biochemically, 55  
 —reducing, estimation of, 24  
**Sulphite cellulose products**, 406  
 —pulp, 84  
 —manufacture of, 88  
**Sulphocyanides**, detection of bromides in presence of, 589  
**Sumac**, 399  
**Sunflower oil**, 140  
**Sylvestrene**, 324  
**Synthetic tans**, 409  
  
**Taka-diastase**, use of, in estimating starch, 71  
**Tallow**, Borneo, 149  
**Tannin**, estimation of, in tea, 529  
 —extracts, 400  
 —materials, 384  
 —colour valuation of, 413  
 —substitutes, 406  
**Tannins**, 384  
 —analysis of, 385  
 —constitution of, 385  
 —detection of, 401  
 —vegetable, 401  
**Tars**, detection of asphalt products in, 278  
 —petroleum in, 278  
 —dimethyl sulphate test for, 278  
**Tartaric acid**, 99  
 —commercial, 101  
 —estimation of, 103  
**Tartars**, London method for, 100  
**Tea**, 528  
 —estimation of caffeine in, 526  
 —colouring matter in, 529, 454  
 —moisture in, 528  
 —Read's test for detecting colour in, 454  
 —seed oil, 134  
 —tannin in, 529  
**Terpinene**, 324  
**Terpineol**, 343  
**Terpinolene**, 324  
**Terpinyl acetate**, 331  
**Thebaine**, 502  
**iso-Thebaine**, 502  
**Thujyl alcohol**, 343  
  
**Thyme oil**, 376  
**Tin**, estimation of in canned foods, 612  
**Trichlorotri-iodolinolenic acid**, 185  
**Trimethylamine and ammonia**, estimation of, 469  
**Tropeines**, detection of, 491  
**Tryptophane**, estimation of, 563  
**Tung oils**, 140  
**Turkey-red oil**, 145  
**Turpentine oil**, 377  
**Turwar bark**, 399  
**Tyrosine**, estimation of, 563  
 —and cystine, separation of, 563  
  
**Urea**, estimation of, 564  
**Uric acid**, 570  
 —estimation of, in blood, 572  
 —urine, 571  
**Urine**, estimation of acetone in, 576  
 —aceto-acetic acid in, 577  
 —lactic acid in, 584  
 —uric acid in, 571  
  
**Valentine's meat juice**, 614  
***d*-Valine and *d*-Alanine**, separation of, 562  
**Vanilla**, 306  
**Vanillin**, 306  
 —detection of, 307  
 —estimation of, 307  
**Vaseline oil**, 259  
**Vegetable tannins**, 401  
**Vetivert oil**, 347  
**Vigoral**, 614  
**Vinegar**, 92  
 —cider, 94  
 —volatile acids in, 92  
 —wine, 94  
  
**Walnut oil**, 145  
**White tan**, 399  
**Wine vinegar**, 94  
**Wines**, 13  
 —estimation of tartaric acid in, 106  
 —volatile acids in, 92  
**Wintergreen oil**, 305, 381  
**Wood-pulp**, 81  
**Wool-grease**, hydrocarbons from, 228  
**Wormseed**, estimation of santonin in, 550  
**Wyeth's beef juice**, 614  
  
**Xanthine bases**, detection of, 525  
**Xylose**, reducing power of, 63  
  
**Yeast**, 15  
**Ylang-ylang oil**, 382  
  
**Zingiberene**, 325



# AUTHORS INDEX

## A

- ABBE.** Refractometer, I, 23
- ABDERHALDEN.** *d*-Alanyl-glycine and *d*-alanyl-glycyl-*L*-tyrosine, VIII, 471  
Amino-acids formed by the hydrolysis of salmine, serum albumin and serum globulin, VIII, 20  
Corpuscles, red, composition of, VIII, 502  
Glycogen, estimation of, VIII, 285  
preparation of, VIII, 281  
Histone of haemoglobin, hydrolysis of, VIII, 506  
Meat, assay of, VIII, 297, 298  
Ptomaines, VIII, 323  
Silk, composition and structure of, VIII, 642  
Tryptophane and hydroxytryptophane, effect of tyrosine reagent on, IX, 563  
and **FUCHS.** Keratin, composition of, VIII, 673  
**FUNK.** Amino-acids formed by the hydrolysis of caseinogen, VIII, 20  
**PREGL.** Amino-acids formed by the hydrolysis of egg-albumin, VIII, 20  
**SAMUELY.** Amino-acids formed by the hydrolysis of serum globulin, VIII, 20  
**SCHITTENHELM.** Casein, composition of, VIII, 121  
**SCHMIDT.** Ninhydrin test for amino-groups, IX, 560  
Proteins, colour test for, VIII, 41  
Silk, composition and structure of, VIII, 642  
**STRAUSS.** Keratins, VIII, 92  
Spongin, VIII, 92  
**WALDER.** Silk, composition and structure of, VIII, 642  
**WIEL.** Amino-acids, esterification of, IX, 561  
Proteins of nervous tissue, hydrolysis of, VIII, 689  
plant, hydrolysis of, VIII, 95  
See also *Diels*, *Fischer*.
- ABEL, FREDERICK (SIR).** Closed oil tester, III, 122
- ABEL.** See *Ladenburg*.
- ABELOUS and GÉRARD.** Nitrates, reduction of, by the direct action of meat, VIII, 363
- ABL.** Uric acid, output of, IX, 571
- ABLETT.** See *Silberrad*.
- ACH and KNORR.** Constitution of codeine, VI, 356
- ACKERMANN.** Cadaverine, VII, 348  
 $\beta$ -Iminazolethylamine, VII, 350  
Marcitine, isolation of, from putrid pancreas, VII, 354  
Putrescine, VII, 347  
Viridinine, isolation of, from putrid pancreas, VII, 353  
and **KUTSCHER.** Physiological action of iminazolethylamine, VII, 350
- ACKERMANN, E.** Phenols, detection of, with Millon's reagent, III, 296
- ADAM, R.** Cocoa, fibre and pentosans in, VI, 697, 708
- ADAMS.** Milk, estimation of fat in, VIII, 148  
and **DORAN.** Opium, smoke, IX, 508
- ADERS.** See *Fischer*.
- ADLER.** Guaiacum test for blood, VIII, 523  
See also *Frans*.
- ADLER, O and R.** Benzidine and malachite-green tests for blood, VIII, 524
- ADOR.** Melting point of phthalic acid, III, 543
- ADRIAN.** Saffron, V, 419
- ADRIAN, M.** Guaiacol, estimation of, in wood-tar creosote, III, 355
- ADRIANI.** India-rubber globules, IV, 105
- ADRIENZ.** Specific gravity of benzene, III, 203
- ADWUJEWSKI.** Detection of ergot in flour, VII, 24
- AGEMA, J.** Purification of commercial chrysophanic acid, V, 228
- AKRENS.** Spartyrine and oxysparteine, VI, 234  
Stavesacre alkaloids, VII, 15  
Styrax liquidus, IX, 298  
and **HETT.** Beeswax, hydrocarbons in, II, 260  
Japan wax, free palmitic acid in, II, 193  
Olive oil, iodine value for, II, 113  
Storax, resinous adulterants in, III, 465
- AIGNAN.** Polarisation apparatus of Schmidt and Hantsch, II, 339
- AIGNAN, A.** Estimation of rosin oil in turpentine oil, IV, 421
- AISINNANN, S.** Separation of hydrocarbons, IX, 230
- AKITT.** See *Mills*.
- ALBAHARY, J. M.** Cocoa and chocolate, estimation of oxalic acid in, IX, 97  
Cocoa-powders, soluble, VI, 690  
Vegetable substances, analysis of, I, 450
- ALBERT.** Zymase in yeast, I, 214
- ALBRECHT and MÜLLER.** Estimation of naphthalene in coal gas, IX, 266
- ALBRIGHT.** See *Winton*.
- ALBU and NEUBERG.** Metabolism of mineral salts in the animal body, VIII, 293
- ALCOCK.** Assay of sodium salicylate, III, 488
- ALDEN and EHLERT.** Estimation of carvone, IV, 215
- ALÉN.** Arachidic acid in rape oil, II, 123
- ALEXANDER, J.** Albuminoids, VIII, 581; IX, 604  
Gelatin, addition of, to cow's milk, VIII, 594  
colloidal character of, VIII, 589  
sulphur dioxide in, VIII, 617  
tests for, VII, 616  
Glue, selection of, VIII, 614  
tests for, VIII, 603, 608
- ALGRAIN, E.** Estimation of nicotine, VI, 240
- ALLBRIGHT and CLARK.** Apparatus for the determination of the spontaneous combustion of oils, II, 38

- ALLEMAN, GELLERT. Creosote oil, composition of, III, 370  
estimation of tar acids in, III, 379
- ALLEMAN, O. Soap, estimation of formaldehyde in, IX, 208
- ALLEN. Acetate of lime, assay of, I, 508, 510  
Alcohol, estimation of, in ether, I, 229  
Arachis oil, arachidic acid from, II, 96  
fatty acids from, II, 93  
Arctic sperm oil, II, 241  
Beer, detection of bitter principles in, VII, 192  
Caffeine, effect of heat on, VI, 582  
estimation of, in tea, VI, 590, 607  
extraction of, VI, 590  
Camphor, specific rotation of, IV, 198  
Carbolic acid, commercial, III, 304, 305  
Castor oil, specific gravity of the mixed acids from, II, 161  
Cinchona alkaloids, titration of, VI, 496  
Cineol, estimation of, in eucalyptus oils, IV, 340  
Cocanut oil, mixed fatty acids from, II, 188  
specific gravity of, II, 188  
Coffee and chicory extracts, specific gravity of, VI, 659  
tinctorial power of infusions of, VI, 677  
detection of starch in, VI, 672  
Colophony, constants for, IV, 26  
Cream of tartar, calcium tartrate in, I, 543  
commercial, assay of, I, 548  
Creosote oil, beechwood, composition of, III, 352, 354  
Cresylic acid, bromo-derivative of, III, 315  
Cyanates, estimation of, VII, 540  
Dinitrophenol, estimation of, in picric acid, III, 583  
Ethyl nitrite, detection of, I, 231, 246  
Fatty acids, higher, constants for, II, 379  
Glycerol from boiled linseed oil, II, 344  
Indicators, III, 552  
Japan wax and its mixed fatty acids, II, 193  
Linseed oil, fatty acids from, II, 350  
Meat extracts, analysis of, VIII, 422  
Metals, estimation of, in canned foods, VIII, 341  
Myrtle wax, constants for, II, 195  
Nitroethane in spirit of nitrous ether, I, 243  
Oils, addition of sulphuric acid to, II, 59  
coefficients of expansion of, II, 50  
fats and waxes, specific gravity of, II, 49  
Oleic acid, II, 408  
Olive oil, fatty acids from, II, 108  
Palm oil, specific gravity of the mixed fatty acids from, II, 184  
Petroleum and shale products, action of bromine on, III, 109  
Phenol, cresylic acid and wood-tar, differentiation between, III, 358  
Porpoise oil, II, 230, 231  
Potable spirits, estimation of higher alcohols in, I, 188  
Rape oil, mixed fatty acids from, II, 124  
specific gravity of, II, 127  
Reichert value for fats and oils, II, 23  
Rosin oil, detection of, III, 174
- ALLEN. Rubber, extraction of, IV, 124  
Saccharin, detection of, I, 164; III, 432  
estimation of, I, 164, 176  
Schiff's reagent, preparation of for the fuchsin test, I, 257  
Shark liver oil, II, 223  
Soap, assay of, II, 426, 432  
Sperm oil, II, 233, 235  
Spermaceti, saponification of, II, 275  
Sugar solutions, specific gravity of, I, 289  
Tea, ash from, VI, 605  
assay of, V, 88  
Tribromophenoxides, III, 299
- and FLETCHER. Estimation of the total astringent matter of tea, VI, 617
- MOOR. Imitation of cider-vinegar, I, 497
- SCOTT, G. E. Colour reactions of ipecacuanha alkaloids, VII, 43
- SCOTT-SMITH. Alkaloids, ipecacuanha and morphine, similarity of colour reactions of, VI, 432  
reaction of with ferric chloride, VI, 201
- SEARLE. Meat extracts, assay of, VIII, 422  
Proteins, precipitation of, VIII, 397
- TANKARD. Estimation of salicylic acid, III, 481
- THOMSON. Unsaponifiable matter in carnauba wax, II, 270
- ALLEN, A. H. See *Alder Wright*.
- ALLEN, L. Asphalt, hard, estimation of, IX, 149
- ALLIEN. Action of dextrose and of levulose on Fehling's solution, I, 374
- ALLIX. Analysis of Caucasian koumiss, VIII, 231
- ALOY. Estimation of morphine, VI, 386  
and RABAUT. Morphine, detection of, IX, 498
- ALSBERG. See *Levene*.
- ALSOP. Analysis of chestnut wood, V, 38, 57
- ALT. Estimation of thiocyanates, VII, 550
- ALTSCHUL. Estimation of salicylic acid in salipyrin, III, 491
- ALVAREZ, E. P. Chrysophanic acid, V, 227  
Triacetyl aconitine, VI, 262
- AMAGAT and JEAN. Use of the oleorefractometer, II, 43
- AMBERG and LOEVENHART. Compounds which retard rennet coagulation, VIII, 130
- AMBÜHL. Estimation of starch in sausage, VIII, 374
- AMERICAN LEATHER CHEMISTS ASSOCIATION. Leather, analysis of, IX, 411  
Tannins, analysis of, IX, 386
- AMERICAN SUBCOMMITTEE on shellac analysis, IV, 70
- AMMAN. See *Lindel*.
- AMOS. See *Salmon*.
- AMSEL, H. Colophony, constants for, IV, 26  
Oils, effect of external influences on the drying of, II, 347  
Resinate driers, value of, IV, 34
- AMTHOR. Caramel, test for, I, 179, V, 639  
Ptomaines which give the strychnine oxidation test, VI, 452
- ANDER, J. J. Action of phloroglucinol on the bones of animals, VIII, 585
- ANDERSON, A. Detection of caramel in vinegar, IX, 96

- ANDES.** Linseed, composition of, II, 325  
Resinate driers, value of, IV, 34
- ANDÉS, L. E.** Identification of Venice turpentine, IV, 77
- ANDOURARD.** Separation of gum arabic and sugar, I, 443.
- ANDOURARD, A. and P.** White spirit, IV, 426
- ANDRÉ.** Separation and estimation of quinine, VI, 513
- ADREASCH, F.** Sumac, adulteration of, V, 103  
Tannin-materials, reactions of, in alcoholic solutions, V, 55  
Tan liquors, fermentation in, V, 98
- ANDREWS.** Alkaloids in *Datura stramonium*, assay of, VI, 320  
Codeine in opium, VI, 395  
See also *Dunstan*.
- ANDREWS, L. W.** Hydrocyanic acid, estimation of, in essential oils, IX, 325  
Phenol, aqueous, melting points of, III, 292
- ANDRIK, K.** Adenine, preparation of, from molasses residues, IX, 568
- ANGELI.** Preparation of azoimide, VI, 27
- ANGELL.** Exhauster for the estimation of oils and fats, II, 5
- ANGELONI.** Aristoquinine and euquinine, IX, 519
- ANNEKER.** Morphine, estimation of, IX, 502
- ANSCHÜTZ.** Acridine, use of, in the estimation of picric acid, III, 581  
Benzaldehyde, preparation of, III, 417  
Chloroform, preparation of, from salicylide, III, 499  
Picric acid, estimation of, VI, 164  
and **LEATHER.** Pipitzahoic acid, V, 230  
**SCHULTZ.** Constitution of primuline, V, 371
- ANTHON, E.** Molasses, table showing the percentage composition of, from the specific gravity of solutions, I, 353
- ANTRICH.** Optical activity of cocaine hydrochloride as a test of its purity, VI, 330
- APPLEYARD.** See *Bastow, Key*.
- ARATA, P. N.** Coal-tar colours, detection of, in food, V, 642; VIII, 382  
Tannin of maté and of coffee, VI, 642
- ARCHBUTT, L.** Arachis oil, analysis of, II, 98  
arachidic acid from, II, 96  
detection and estimation of, II, 93  
specific gravity of the fatty acids from, II, 93  
Beeswax, acid and saponification values for, II, 253  
hydrocarbons in, II, 260  
Carnaúba wax, unsaponifiable matter in, II, 270  
Castor oil, solubility of, in alcohol, II, 162  
Cocanut olein, constants for, II, 191  
Cottonseed oil, silver nitrate test for, II, 137  
Curcas oil, II, 174  
solubility of, in alcohol, II, 173  
Lard oil, acidity of, II, 198  
Linseed oil, specific gravity of the fatty acids from, II, 350  
Maize oil, drying properties of, II, 140  
viscosity of, II, 140  
Mustard oil, II, 120
- ARCHBUTT, L.** Oils and fats, bromine thermal process for, II, 61  
and waxes, examination of, II, 91  
fixed, addition of sulphuric acid to, II, 59  
Olive oil, arachidic acid in, II, 108  
elaidin test for, II, 116  
free fatty acid in, II, 10  
oleic acid in, II, 109  
heat of bromination of, II, 116  
iodine value for, II, 113  
saponification value for, II, 115  
specific gravity of the mixed fatty acids from, II, 108  
Olive oils, saponified, IX, 132  
Tunisicin, estimation of, II, 95  
Palm oil, palmitic acid in, II, 185  
specific gravity of the mixed fatty acids from, II, 184  
Poppseed oil, II, 153  
Poutet's elaidin test for fixed oils, modification of, II, 39  
Rape oil, arachidic and lignoceric acids in, II, 123  
constants for, II, 124  
solidifying point of, II, 123  
specific gravity of, II, 127  
the mixed fatty acids from, II, 124  
Rosin grease, formation of, from rosin oil, IV, 47  
Soja bean oil, II, 147  
Sperm oil, alcohols from, II, 234  
Tallow, free oleic acid in, II, 209  
oil, II, 202  
specific gravity of the fatty acids from, II, 209  
Turpentine oil, distillation of, IV, 413  
iodine absorption of, IV, 423, 424  
rotation of, IV, 406  
specific gravity of, IV, 408  
Whale oil, specific gravity of the fatty acids from, II, 229
- and **DEELEY.** Castor oil, absolute viscosity of, II, 162  
behavior of, with petroleum spirit, II, 163  
solubility of, in alcohol, II, 162  
Lubricating greases, water in, III, 179  
Porpoise oil, II, 231  
Rape oil, commercial, free acid in, II, 125  
Rosin grease, analysis of, IV, 47  
Sperm oil and arctic sperm oil, constants for, II, 236  
fatty acids from, II, 235  
Waxes, unsaponifiable matter from, II, 26
- REDWOOD.** Specific gravity of rape oil, II, 127
- ARCHETTI.** Action of ferric chloride on glycerol, II, 452
- ARKIN.** Assay of opium, VI, 426
- ARMANI, G. and RODANO, G. A.** Ceresin, and paraffin, separation of, IX, 258
- ARMANNI.** See *Malagnini*.
- ARMITAGE, J. L.** Test for morphine, VI, 379
- ARMSTRONG, E. F.**  $\alpha$  and  $\beta$  dextroses, differentiation between, in glucosides, I, 392  
Enzymes, VIII, 1; IX, 591

- ARMSTRONG, E. F.** Flour, IX, 593  
 Glucosides, VII, 95; IX, 545  
 Polarimetric work, use of emulsin in, VIII, 6  
 Proteins of plants, VIII, 93  
 Starch and its isomerides, I, 405  
 Sugar, identification of, in glucosides, I, 392  
 Sugars, I, 285  
   estimation of with Pavy's solution, I, 332  
 Sugars, measurement of the hydrolysis of, VIII, 8  
 Yeast, species of, which do not ferment maltose, I, 362  
 See also *Kesble*.  
 and **LOWRY, T. M.** Birotation, I, 315  
**ARMSTRONG, H. E.** Camphor,  $\beta$ -derivatives of, IV, 202  
 Fulminic acid, formula of, VII, 542  
 Triphenylmethane dyestuffs, quinonoid structure of, V, 238  
 Turpentine oil, IV, 405  
   estimation of petroleum naphtha in, IV, 414  
   rotation of, IV, 406  
 and **EYRE.** Detection of hydrocyanic acid in flaxseeds, IX, 183  
**HORTON.** Estimation of urea, VII, 302  
**ROSSITER.** Nitro-derivatives of the naphthols, III, 253  
**TILDEN.** Optically inactive borneol, IV, 278  
**ARNAUD.** Carotol from beets, II, 485  
 Ouabain, VII, 123  
**ARNDT.** Alkaloids in ipecacuanha, VII, 48  
 Choline in ipecacuanha root, VII, 41  
**ARNOLD.** Atropine, test for, VI, 306  
 Kjeldahl-Gunning estimation of nitrogen, I, 62  
 Margarine and lard, saponification values of, II, 287  
 Milk, heated, detection of, VIII, 168  
 See also *Grimaux*.  
 and **MENTZEL.** Caviare, identification of, IX, 622  
 Milk, heated, detection of, VIII, 168  
 Yeast and meat extracts, distinction between, VIII, 416  
**ARTHUR and PAGE'S.** Action of rennet enzyme, VIII, 129  
**ARTHUS.** Solubility of casein in salts, VIII, 124  
**ASBOTH.** Butter and margarine, critical temperature of solution for, II, 64  
 Lard and cottonseed oil, iodine values of, II, 392  
**ASCHAN and HJELT.** Finland turpentine oil, IV, 402  
**ASCHER.** Assay of opium, VI, 426  
**ASHBY, A.** Detection of free mineral acids in vinegar, I, 503  
**ASHWELL, J. R. and FORTH, H.** Poisonous metals in colouring matters, V, 478  
**ASTRUC.** Acetyl salicylic acid, estimation of, IX, 306  
 Alkaloids, use of methyl orange in the estimation of, VI, 182  
 phenolphthalein in the estimation of, VI, 181  
 rosolic acid in the estimation of, VI, 182  
**ASTRUC.** Glycerophosphates, estimation of, II, 452  
 and **CAMBE.** Syrup of Tolu balsam, III, 461  
**PÉGURIER.** Estimation of pyramidone, VI, 49  
**ATAK.** Detection of hardened fats in margarine, IX, 173  
**ATENSTADT.** See *Beythien*.  
**ATHANASESCU.** See *Pictet*.  
**ATKINS.** Detection of the addition of water to milk by the freezing point, VIII, 166  
**ATTFIELD.** Alkaloids, percentage of, in ipecacuanha, VII, 48  
 Tin in canned foods, VIII, 338, 339  
**ATWATER, W. O.** Composition of the flesh of fish, VIII, 457  
 See also *Bryant*.  
 and **BRYANT.** Eggs, analyses of, VIII, 439  
 Meat, composition of, VIII, 262  
   canned, analyses of, VIII, 336  
**AULD.** Linseed cake, II, 326; IX, 182  
 See also *Danstan, Henry*.  
**AUTENRIETH.** Detection of hydrocyanic acid in the presence of potassium ferrocyanide, VII, 468  
 and **BEUTTEL.** Estimation of salicylic acid, IX, 303  
**AVERILL.** See *Gaylord*.  
**AVERY.** See *White*.  
**AWENG.** Gallotannic acid, IX, 385  
 See also *Tschirck*.  
**AXELROD.** Rubber, acetone extraction of, IV, 124  
 Vulcanised rubber, analysis of, IV, 130, 134  
**AYKROYD.** See *Richardson*.
- B**
- BABCOCK.** Cream, estimation of fat in, VIII, 187  
 Milk, analysis of, VIII, 163  
   use of hydrogen peroxide as a preservative for, VIII, 691  
**BABEL.** Conversion of oxyhaemoglobin to methaemoglobin, VIII, 540  
**BABKIN.** Gastric juices, acidity of, IX, 580  
**BACH.** Guaiacol as an oxydase reagent, IX, 591  
 Medicine, detection of bitter principles in, VII, 137  
 Oxydase, estimation of, VIII, 14  
 Tyrosinase, estimation of, VIII, 14  
 and **CHODAT.** Estimation of oxydase, VIII, 14  
**BACH, A.** Determination of the gumming quality of lubricating oils, III, 159  
**BACHMAN, W.** Jellies, ultramicroscopic structure of, IX, 604  
**BACON.** Champaca oil, IX, 357  
 See *Bigelow, Lindall*.  
**BACON, R. F.** Ylang-ylang oil, IX, 383  
 See also *P. B. Dunbar*.  
**BAESSLER.** Pyridine, estimation of, in presence of ammonia, IX, 476  
**BAEYER.** Carvestrene, IV, 179  
 Euxanthic acid, VII, 395  
 Homolka's base, V, 235  
 Hydrophthalic acids, III, 543  
 Indigo, synthesis of, V, 390  
 Terpenes, IV, 166

- BAEYER and VILLIGER.** Diphenylaminofuchsone-phenylimine, v, 236
- BAGARSKY.** See *Liebermann*.
- BAGINSKY.** Isolation of xanthine, vi, 580
- BAILEY.** See *Winton*.
- BAINBRIDGE and MORROW.** Aloes, tests for, vii, 145
- BAKER.** Tin, estimation of, in canned foods, ix, 612  
See *Ling*.
- SMITH.** Eucalyptus oils, iv, 338, 339, 341
- BAKER, H. A.** Canned meat, viii, 331, 333
- BAKER, JULIAN L.** Malt and malt liquors, i, 133  
Malt substitutes, extract of, i, 144  
Sugar in coffee, vi, 645  
and **DAY.** Preparation of pure maltose, i, 361  
**DICK.** Hops, effect of sulphur fuel on the arsenical contamination of, vii, 185  
Maltose, estimation of, i, 365, ix, 53  
**HULTON, H. P. E.** Infants' foods, analysis of, viii, 233  
Malt and barley, wasted, and malt wort, colour of, i, 135, 143  
**POPE.** Detection of sugar in coffee, vi, 645
- BALAVOINE.** Detection of poppy oil in walnut oil, ii, 159
- BALBIANO.** Synthesis of pyrazolone, vi, 35  
and **PAOLINI.** Test for olefines, ix, 234
- BALKER.** Isolation of xanthine bases from flesh and malt, vii, 326
- BALL, HANDBY.** Constants for Irish butter fats, ii, 285  
See *White*.
- BALLAND.** Proteins in leguminous foods, viii, 96
- BALLANTYNE.** Linseed oil, effect of light and air on the iodine value of, ii, 335  
specific gravity of, ii, 330, 331  
free fatty acids in, ii, 333  
See also *Thomson*.
- BALLS.** Reduction of nitrobenzene with magnesium ribbon, iii, 213
- BALZER.** See *Tschirch*.
- BAMBERGER.** Resins, methoxyl-values of, iv, 10, 15  
Sparteine, boiling point of, vi, 232  
See also *Gregor*.
- BANG.** Nucleoprotein of the lymphatic organs, viii, 92  
Rennet-enzyme, viii, 126  
Sugar solutions, analysis of, i, 335
- BANNER.** Turpentine substitute, iv, 426
- BANNO.** Formation of nitrosamines from secondary amines, vi, 9
- BARAGIOLA and SCHUPPLI.** Lactic acid, estimation of, ix, 584
- BARBIER.** Licarhodol, iv, 262  
*d*-Linalol in coriander oil, iv, 332  
and **BOUVEAULT.** Citronellol, ix, 341  
constitution of, iv, 263  
Rose oil, alcohol in, iv, 383  
**LÄSER.** Citronellol, ix, 341  
**LOCQUIN.** Citronellol, ix, 341
- BARBIER, E.** Isolation of alcohol in essential oils, iv, 246
- BARBIER, P.** Effect of heating geraniol with strong alcoholic potash, iv, 260
- BARBIERI.** Colouring matter of eggs, ix, 620  
See also *Schulze*.
- BARCROFT.** Estimation of hæmoglobin, viii, 560  
and **A. U. HILL.** Heat of combination of hæmoglobin and oxygen, viii, 522
- ROBERTS.** Carboxyhæmoglobin, estimation of, in blood, viii, 533  
Hæmoglobin, saturation of, with oxygen, viii, 522
- BARDACH and SILBERSTEIN.** Estimation of sugars, ix, 56
- BARDET.** Chloral antipyrine, vi, 46
- BARDY.** See *Riche*.
- BARENTHIN.** Iodine value of essential oils, iv, 239, 240
- BARFORD.** Dextrose, test for, i, 333  
Resin and fatty acids, separation of, iv, 33
- BARGELLINI.** Glucosides, synthetic, ix, 545  
See also *Francesconi*.
- BARGER, G.** Carpaine, constitution of, vii, 2  
Ergot, formation of *p*-hydroxyphenyl-ethylamine in, vii, 346  
Hordenine, synthesis of, vii, 36  
Ptomaines, vii, 341  
Vegetable alkaloids, vii, 1  
and **CARR.** Ergotoxine, vii, 16
- DALE.** Cadaverine, physiological action of, vii, 349  
Ergot alkaloids, vii, 16  
Ergotoxine, physiological properties of, vii, 23  
Iminasolyethylamine, vii, 350  
Isoamylamine, physiological action of, vii, 345  
*β*-phenylethylamine, physiological action of, vii, 346
- EWINS, A. J.** Alkaloids, vegetable, ix, 534  
Ergothioneine, vii, 21  
Ergotoxine, esterification of, vii, 19
- FIELD.** Oxidation of aconitine, ix, 487
- WALPOLE.** *p*-Hydroxyphenylethylamine as a putrefaction product, vii, 346  
synthesis of, vii, 347  
Isoamylamine as a putrefaction product, vii, 345  
*β*-phenylethylamine in putrid horse meat, vii, 346
- BARILLOT, E.** Test for colchicine, vii, 5
- BARNELY, O. L.** Cyanides, detection of, ix, 585
- BARNES and LIDDLE.** Estimation of thiocyanates, vii, 554
- BARNSTEIN.** Estimation of proteins, viii, 52
- BARON.** Artificial dégras, ii, 505
- BARONI and BORLINETTO.** Hydrastine, reaction of, ix, 522
- BARR, G.** See *H. J. H. Fenton*.
- BARRACLOUGH, W. H.** Test for morphine, vi, 380
- BARRAL, E.** Phenacetin and acetanilide, distinction between, vi, 101  
Salicylic acid, tests for, ix, 300
- BÂRREME.** Lavender oils, ix, 363
- BARROWCLIFF,** American pennyroyal oil, iv, 377  
and **TUTIN.** Resolution of atropine into *d*- and *l*-hyoscyamine, vi, 295
- BARSHALL, H.** See *E. Baur*.



- BERNEGAU and HEIDLBURG. Morphine, estimation of, IX, 508
- BERNHART. Ergot in flour, VII, 24
- BERNHEIMER, O. Roasting of coffee, VI, 649
- BERNTSEN, A. Blue sulphide dyestuffs from methylene violet, V, 379
- BERRÁR. Gelatin, separation of, IX, 605
- BERRY. Reactions of natural colours on mordanted wool, V, 636  
See *Winton*.
- BERRY, W. G. Resins of gutta-percha, IV, 159
- BERTAINCHAUD. See *Milliau*.
- BERTARELLI. Addition of borax to coffee, VI, 668
- BERTÉ and GULLI. Detection of adulterants in tangerine orange oil, IV, 363
- BERTHEAUME. Separation and estimation of methylamines and ammonia, VI, 18
- BERTHELOT. Boiling point, determination of, I, 17  
Bitumens, origin of, III, 37  
Ethyl alcohol, detection of, in wood naphtha, I, 103  
Fractional distillation, I, 19  
Indicators, behaviour of various, III, 552  
and WERNER. Thermo-chemical experiments on polyphenols, III, 341
- BERTHELOT, M. Oxidation of pyrogallol, III, 537
- BERTRAM. Production of vanillin from eugenol, III, 515  
and GILDEMEISTER. Alcohols in rose oil, IV, 383  
WALBAUM. Camphene, detection of, in oils, IV, 278  
French oil of lavender, composition of, IV, 347  
Pine-needle oils, IV, 379
- BERTRAND. Caffeine in coffee, VI, 657  
Enzymes, measurement of the increase of reducing power by, VIII, 7  
Essence of niaouli, IV, 319  
Quinol test for oxydases, VIII, 13  
Sugars, estimation of, IX, 24  
Vicianin, VII, 103  
and DUCHÁČEK. Estimation of sugars biochemically, IX, 56  
JAVILLIER. Nicotine, estimation of, IX, 485  
Silicotungstic acid, use of, as a precipitant for alkaloids, IX, 479  
WEISWEILLER. Sugars, estimation of biochemically, IX, 56  
Roasted coffee, aroma of, IX, 530
- BESSON. Estimation of lactic anhydride in commercial lactic acid, VII, 441, 442
- BESSON, A. Estimation of fatty acids in soap, IX, 206
- BESSON, A. A. Analyses of tea, VI, 601
- BESTHORN. See *O. Fischer*.
- BEUTTEL. See *Autenrieth*.
- BEVAN. Silver nitrate test for cottonseed oil, II, 137  
See also *Cross*.  
and CROSS. Determination of the softening point of fats, II, 53
- BEYERINCK. Culture yeast, I, 216  
Maltase in yeast, I, 211
- BEYERINCK. Proteolytic enzyme in yeast, I, 212
- BEYS. Estimation of glycerol in wines, IX, 221
- BEYTHIEN and ATENSTADT. Analysis of mouth-washes, III, 498  
BOHRISCH and DEITER. Estimation of the extract from tea, VI, 622
- BIANCHI and DI NOLA. Saccharin, detection of, in foods and beverages, III, 432  
isolation of, from fatty oils, III, 433
- BIANCHINI, G. See *F. Casoneri*.
- BIBERFELD. Glycuronic acid, IX, 575
- BICKERN. Casimirol, II, 488
- BIDET, A. Action of light on aniline and toluidine, VI, 54
- BIEL, J. Fractional distillation of mineral burning oils, III, 128
- BIERLING. See *Schulze*.
- BIERNATH. Detection of benzoic acid in butter, IX, 282
- BIERRY and GRUZEWSKA. Estimation of glyco-gen, IX, 608
- HAZARD and RANC. Sugar content of eggs, IX, 620
- BIGELOW. Cinnamic acid, estimation of, III, 438  
Salicylic acid, estimation of, in wine, III, 483  
Wines, analysis of, I, 165  
estimation of sulphurous acid in, I, 174  
and BACON. Tin in canned foods, VIII, 339
- COOK. Caseoses, estimation of, in peptonised milk, VIII, 220  
Meat bases, estimation of nitrogen in, VIII, 301  
extracts, analyses of, VIII, 401, 402  
estimation of peptones in, VIII, 409  
composition of, VIII, 397  
manufacture of, VIII, 395  
yeast extracts as an adulterant of, VIII, 416  
Peptones, estimation of, VIII, 397, 409
- MCILROY. Determination of sugars in milk, I, 370
- MUNSON. Estimation of metals in canned foods, VIII, 342
- BIGGS. See *Scudder*.
- BIGINELLI. Aristoquinine, IX, 519  
Kerner test for quinine sulphate, VI, 521
- BIGINELLI, P. Quinine tannate, VI, 530
- BIGNAMI and TESTONI. Parsley oil, IV, 369
- BIGNON, A. Cocaine benzoate, VI, 327
- BIGNON, M. Alkaloid in coca leaves, VI, 351
- BILLON. Estimation of glycerol in wines, I, 167
- BILTZ. White Peru balsam, III, 455
- BINEAU. Preparation of ammonium cyanide, VII, 472
- BING. Copper in rubber goods, IV, 138
- BINZ and RUFFERATH. Estimation of indigotin by reduction with sodium hydrosulphite, V, 400  
and RUNG. Estimation of indigo, IX, 428
- BIRCKENSTOCK. Hybridisation of true and spike lavender flowers, IX, 363
- BIRD. Assay of belladonna plaster, VI, 315  
Filter tube for use in the estimation of alkaloids with Mayer's reagent, VI, 193

- BIRD, F. C. J. Estimation of morphine in paregoric, VI, 431
- BISCHOFF and NASTVOGEL. Dry distillation of colophony, IV, 36
- BISHOP. Furfuraldehyde test for sesame oil, II, 144  
 Linseed oil, rotation of, II, 338  
 Oils, determination of the drying properties of, II, 38  
 Olive oil, rotation of, IV, 198
- BITTO. Sodium nitroprusside test for ketones, VII, 531
- VON BITTO, B. Extraction of lecithin by Schulze's process, VII, 283
- BLACK.  $\beta$ -hydroxybutyric acid, IX, 578
- BLACK, J. W. See *T. Cockburn*.
- BLACKADDER, T. See *J. Walker*.
- BLACKLER, M. BENNETT. Resins, IV, 1
- BLAISE. Chamomile oil, Roman, IV, 328
- BLAKE. Occurrence of asphalt, III, 58  
 See *Bates*.
- BLAKEMAN. Patent drying oil, II, 157
- BLANK and FINKENBEINER. Formaldehyde, estimation of, by the hydrogen peroxide method, I, 261  
 Methyl alcohol, estimation of, in formaldehyde, I, 93
- BLANKSMA, J. J. See *W. Alberdavan Ekenstein*.
- BLAREZ, C. Test for red coal-tar dyes, V, 250
- BLATHERWICK. Urine, composition of, IX, 571
- BLAU. Extraction of colchicine, VII, 9
- BLENN, P. Coagulation of egg-albumin, VIII, 434
- BLOCH. See *Dunstan*.
- DE BLOEME, SWART and TERWEN. Colloidal nitrogen in urine, IX, 575
- BLOXAM. Indigotin, estimation of, V, 394  
 Potassium ferricyanide, reduction of, VII, 526  
 Strychnine, colour reactions for, VI, 453  
 See *Gawn*.
- BLOXAM, C. L. Bromine as a reagent for alkaloids, VI, 189
- BLOXAM, W. P. Indigotin tri- and tetrasulphonic acids, V, 388  
 See *A. G. Perkin*.
- and PERKIN. Extraction of indirubin, V, 397
- BLUM and FIELD. Measurement of rennin hydrolysis, VIII, 11
- and FULD. Estimation of the proteoclastic power of pepsin, VIII, 494
- BLUMANN and ZEITSCHEL. Nerol, IX, 342
- BLUME, G. See *M. Busch*.
- BLUMENFELD. See *Schneider*.
- BLUMENFELD and SEIDEL. Coconut oil, composition of, II, 188  
 Palm-nut oil, volatile fatty acids in, II, 195
- BLUMER. See *Gnehm*.
- BLUNT, T. P. Assay of ipecacuanha, VII, 45
- BLYTH, A. W. Cocoa-red, VI, 699  
 estimation of, VI, 710  
 Caffeine, sublimation of, VI, 582  
 Frogs, sensitiveness of, to picrotoxin, VII, 163  
 Logwood test for alum in flour, I, 457  
 Milk, detection of colouring matter in, V, 660  
 Muscarine, detection of, in cases of poisoning, VII, 286  
 Pepper, VII, 57
- BLYTH, A. W. Subliming point, determination of, I, 17  
 Sugar, estimation of, with Pavy's solution, I, 332  
 Tea, detection of foreign leaves in, VI, 632  
 Tin in canned fruit, VIII, 338  
 Wheat ash, mineral constituents of, I, 456  
 Wheaten bread, analyses of, I, 459  
 Wines, detection of artificial colour in, V, 655
- and ROBERTSON. Glyceryl stearo-palmito-butyrate in butter fat, II, 280
- BOAS, J. Paraphenylenediamine hydrochloride test for blood, VIII, 525
- BOASSON. See *Nöbling*.
- BOCKFONTAINE. See *S&c*.
- BOCKLISCH. Methylamine, presence of, in putrid fish, VII, 345  
 Methyl-guanidine from impure cultures of *vibrio proteus* in beef-broth, VII, 306
- BODENBENDER. Percentage of nitrogen in beet-root molasses, I, 356
- BODNER. See *Stokes*.
- BÖCKER and HAHN. Pine needle oil, IX, 372
- BOEDECKER. Berberine, VI, 552
- BÖDEKER. See *Fischer*.
- BOEGH. Estimation of tannins, V, 90
- BÖHMER, C. Mode of occurrence of nitrogen in various vegetables, VII, 238
- BOEHRINGER and SÖHNE.  $\beta$ -Chloromorphide, VI, 389  
 Lactic acid, impurities in, VII, 443
- BOEKHOUT and DE VRIES. Lactic acid in cheese, VIII, 247
- BÖLSING. See *Verley*.
- BOEMER. Unsaponifiable matter of linseed oil, IX, 188
- BÖMER. Beef and mutton tallow, composition of, II, 208  
 Lard, detection of beef and mutton fats in, IX, 178  
 Nickel, detection of, in hardened oils, IX, 124  
 Phytosterols from various oils, II, 486  
 See *Baumann, King, Uffelmann*.
- and LESCHLY-HANSEN. Examination of hardened oils, IX, 123
- BÖMER, A. Precipitation of albumoses, VIII, 397
- BOESEKEN and WATERMAN. Estimation of salicylic acid, IX, 301
- BOETTINGER. Gallotannic acid, IX, 385  
 Linseed oil, extraction of, from paint, II, 329
- BÖTTINGER. Formula of quercitannic acid, V, 26
- BÖTTINGER, C. Fehling's solution, reduction of by gallic acid, III, 529  
 Gallotannic acid, purity of, V, 22
- BÖTTLER. Melting point of mastic, IV, 59
- BOGGS. Estimation of India rubber, IX, 321
- BOHR. Saturation of hæmoglobin with oxygen, VIII, 522
- BOHRISCH. Detection of acetone in urine, I, 106  
 See *Beythien*.
- and RICHTER. Buchner number for beeswax, II, 256
- BOKORNY, T. Germicidal properties of cinnamic acid, III, 437
- BOLAS. Boiling point of glycerol, II, 447

- BOLDYRELF.** Gastric juices, acidity of, IX, 580
- BOLLEY.** Cultivation of flax, IX, 180
- BOLTON, E. R. and REVIS, C.** Cacao butter and its substitute, distinction between, IX, 150  
Fats, oils and waxes, IX, 126  
See *Cecil Revis*.
- BOMER.** Sesame oil, II, 142
- BONAMARTINI.** Detection of saccharin in foods and beverages, III, 432
- BONANNO.** Bile pigments, test for, IX, 580
- BOND, C. O.** Preparation and testing of pure pentane, III, 112
- BONDI.** Sericin, VIII, 92  
and MÜLLER. Synthesis of glycocholic acid, VII, 411
- BONDZINSKI, DOMBROWSKI and PANEK.** Oxy-proteic acids in urine, VII, 407
- BONENKAMP and VON ELK.** Occurrence of hydrocyanic acid in tropical plants, VII, 462
- BONGAULT and MOUCHEL-LA-FOSSE.** Estimation of cinnamic acid, IX, 292
- BONNET.** Formaldehyde, detection of, I, 258; VIII, 171
- BOOLE.** See *Dunstan*.
- BOOTH, N. P.** Cacao beans, roasting of, VI, 686  
Chocolate, analyses of, VI, 694, 695  
Cocoanibs, analyses of, VI, 687  
See *Miniati*.
- BORDAS.** Alkalis in cocoa, VI, 704  
and DE RACZKOWSKI. Estimation of glycerol in wines, I, 168
- BORLINETTO.** See *Baroni*.
- BORNTRÄGER.** Test for aloe, VII, 144
- BORNTRÄGER, H.** Gutta-percha, IV, 158, 160
- BORSHARD, E. and HUGGENBERG, W.** Estimation of free alkali in soap, IX, 207
- BOSELEY.** See *Richmond*.
- BOSETTI, E.** Veratridine, formula for, VII, 76  
Veratrine, composition of, VII, 72
- BOSSHARD.** See *Schulze*.
- BOSWORTH and VAN SLYKE.** Ash-free casein, IX, 595  
See also *Van Slyke*.
- BOTHAMLEY, C. H.** Absorption spectra of eosins, V, 297
- BOTSCH.** Constitution of caffeol, VI, 650
- BOTTINGER.** Estimation of glycerol in wines, I, 168
- BOUCHARDAT.** *d*-Camphene in lavender oil, IV, 348  
Spike-lavender oil, composition of, IV, 350  
Terpineol, preparation of, IV, 280  
and TARDY. Russian anise oil, IV, 311
- BOUCHER and DE BOUNGE.** Detection of saccharin in foods and beverages, III, 432
- BOUDET.** Estimation of tannins, V, 93
- BOUGAULT.** Estimation of salicylic acid, III, 483
- BOUGHTON.** Linseed-oil ash, IX, 187, 197
- BOUGNAULT, J.** Solubility of picric acid, V, 123
- BOUTLLER.** See *Levene*.
- BOULEZ.** Estimation of alcohols in essential oils, IV, 228; IX, 328, 329
- DE BOUNGE.** See *Boucher*.
- BOURGEOIS.** See *Schützenberger*.
- BOURGOIN.** Solubility of salicylic acid, III, 466
- BOURQUELOT.** Glucosides, detection of, I, 391  
Guaiacol test for oxydases, VIII, 13  
Keratin, use of, for coating pills, VIII, 676  
Keratoids, composition of, VIII, 673  
Meconic acid, detection of, in paregoric, VI, 431  
 $\alpha$ -Naphthol test for oxydases, VIII, 13  
Phenol test for oxydases, VIII, 13
- BOUSFIELD and LOWRY.** Purification of acetic acid, IX, 90
- BOUSSINGAULT.** Asphalt, investigation of, III, 59  
Cocoa nibs, analysis of, VI, 689
- BOUVEAULT.** See *Barbier*.  
and GOURMAND. Citronellol, IX, 341
- BOWMAN.** Tussah silk, microscopic appearance of, VIII, 641  
Wool and hair, structure of, VIII, 677  
microscopic characters of, VIII, 681  
Wool-keratin, VIII, 684
- BOWSER, E. H.** Specifications for creosote oils, III, 369
- BOYER.** Estimation of mineral matter in the ash of commercial cane sugar, I, 346
- BOYVEAU, M.** Artificial oil of bitter almonds, III, 421
- BRACOUNOT.** Ammoniacum, IV, 91
- BRADLEY, C. E.** See *H. U. Tarter*.
- BRADSHAW.** See *La Wall*.
- BRADY.** Oxidation of aconitine, IX, 487
- BRAITHWAITE.** See *White*.  
and FARR. Assay of opium, VI, 424
- BRANDENBURG.** Potassium in red corpuscles, VIII, 503
- BRANDER.** See *Cowie*.
- BRANDL.** Agrostemmic acid, VII, 128
- BRANDT.** Estimation of indigotin, V, 392
- BRANNT.** Asafoetida oil, IV, 95  
Linseed oil and cake, analyses of ash from, II, 332  
Osokerite, III, 55
- BRASS.** Terpenes, IV, 166
- VON BRAUN.** Cadaverine, formation of, from piperidine, VII, 348  
Conium alkaloids, separation of, VI, 221
- BRAUTIGAM and EDELMANN.** Detection of horse flesh in sausages, VIII, 377
- BRAUTLECHT.** See *Osborne*.
- BREINL.** Detection of magenta in orchil and cudbear, V, 428  
See *Reichl*.
- BREMER, H.** Horse flesh, detection of, VIII, 379  
Sausage, detection of cochineal-carmine in, VIII, 381
- BRETEAU.** See *Caseneuve*.
- BRETH, F.** Transformer oils, IX, 256
- BRETONNIÈRE.** See *Croissant*.
- DE BREVANS, J.** Detection of benzoic acid in food, III, 411
- BREWER.** See *Orndorff*.
- BRIAND.** Detection of abastol, III, 403
- BRIANT.** Malt substitutes, determination of extract from, I, 144  
Hop seeds, crushed, VII, 173  
Hops, preservation of, VII, 169

- BRIANT and HARMAN.** Effect of the presence of crushed seeds on the estimation of resins in hops, VII, 177
- MEACHAM.**  $\gamma$ -Resin from hops, VII, 168  
Resins in hops, estimation of, VII, 175  
Tannin in hops, VII, 188
- BRIDGMAN, J. A.** See *G. E. F. Lundell*.
- BRIEGER.** Ptomaines, VII, 341  
Putrefaction bases, VII, 352  
from culture of pathogenic bacteria, VII, 354
- BRIEGER, L.** Preparation of potassium phenyl sulphate, III, 400
- BRIGGS.** Measurement of the handle of paper, IX, 88  
See *Bergthell, Cross*.
- BRIOUX.** Estimation of dicyanamide, VII, 558
- BRISSON.** See *Schrötter*.
- BRIX and GERLACH.** Specific gravity of solutions of cane sugar, I, 289
- BROADBENT.** Effect of the inhalation of hydrocyanic acid on frogs, VII, 466
- BROCK.** See *Redman*.
- BRÖMSTEIN, E.** Aniline, reduction of, VI, 57  
*p*-Toluidine, oxidation products of, VI, 65
- BROMEIS.** Purification of oleic acid, II, 403
- BROOK.** See *Hopkins*.
- BROOKS.** *Bassia mottleyana*, IX, 149  
Champaca oil, IX, 358
- BROOKS, R. O.** Estimation of tartaric acid in cream of tartar, IX, 103
- BROWN.** Properties of aloins, VII, 139  
See *Cripps, Dunstan*.
- BROWN, A. J. and CLUBB, D.** Hops, antiseptic power of, IX, 552, 553  
estimation of antiseptic power of, IX, 558  
and **WARD.** Direct estimation of the antiseptic power of hops, VII, 179
- BROWN, H. E.** Morphine, VI, 439
- BROWN, H. T.** Estimation of amino-nitrogen in protein digestion products, VIII, 486  
Estimation of starch, I, 423  
Nitrogenous constituents of malt, VIII, 105  
Specific gravity of solutions of dextrin, I, 289  
and **HERON.** Calculation of specific rotatory power and cupric reducing power of sugars, I, 304  
Reducing power of maltose, I, 362, 570  
Specific gravity of sugar solutions, I, 289
- MILLAR.** Starch, estimation of, in plant material, IX, 75  
Specific rotatory power of sugars, I, 306  
Tyrosine, estimation of, VIII, 87
- MORRIS.** Pentoses, estimation of, in plant extracts, IX, 66  
Plant extracts, analysis of, IX, 46  
Tannin, effect of, on the activity of enzymes, VIII, 2
- MORRIS and MILLAR.** Cupric reducing power of maltose, I, 570  
Reducing sugars, estimation of, IX, 24  
Refractometer values for sugar solutions, IX, 21  
Specific gravity, determination of, at various temperatures, I, 6  
Starch, estimation of, in cocoa, VI, 712
- MORRIS and MILLAR.** Sugars, solution densities of, IX, 19
- BROWNE.** Fatty acids from butter fat, II, 280
- BROWNE, C. A.** Colorimetric test for invert sugar in honey, I, 386  
Composition of American honeys, I, 383
- BROWNSCOMBE, W. J.** Eucalyptus oils, IV, 337
- BROWNSDON.** Examination of caps, III, 586
- BRUCE, J.** See *R. Willstätter*.
- BRÜCKE.** Extraction of glycogen, VIII, 376  
See *Beckurts*.
- BRÜNING.** See *Meister*.
- BRUGER.** See *Meyer*.
- BRUGIÈRE.** See *Lindel*.
- BRUHL.** Camphene, occurrence of, IV, 182  
Fustic extract, detection of adulteration in, V, 411  
Terpenes, IV, 166
- BRUHNS, G.** Adenine, separation of, from allied bases, VII, 337  
Xanthine and guanine, separation of, from hypoxanthine and adenine, VII, 323
- BRUNCK.** Synthetic indigo, V, 390
- BRUNNER.** Detection of saponins in beverages, VII, 129
- BRUNNER, A.** Solubility of coal-tar dyes in water and alcohol, V, 444
- BRUNTON, T. LAUDER.** Poisoning by brucine, VI, 465
- BRUYLANTS.** Aldehydes, estimation of, in essential oils, IV, 234  
in oil of lemon, IV, 234  
Potassium thiocyanate, presence of, in saliva and urine, VII, 543
- BRUYLANTS, G.** Meat extracts, analysis of, VIII, 397  
Peptones, analysis of, VIII, 396
- BRUYLANTS, J.** Analysis of meat extracts, VIII, 420
- DE BRUYN, LOBRY.** Hydrazine, preparation of, VI, 24  
Rubber mixings, IV, 120  
and **VAN EKENSTEIN.** Glucose, IX, 50
- BRYANT.** See also *Atwater*.  
and **ATWATER.** Proteins in plants, VIII, 95
- BRYKNER.** See *Wagner*.
- BRYLINSKI.** Indigo, estimation of, IX, 428  
Indigotin, estimation of, V, 393
- BUCHERER.** Constitution of aniline black, V, 316
- BUCHHOLZ.** Ammoniacum, IV, 91
- BUCHNER.** Beeswax, action of ether on, II, 243  
determination of the saponification value of, II, 253  
effect of bleaching on the constants of, II, 245  
test for, II, 256  
Berberine, VI, 551  
Gambogic acid, formula of, V, 416  
Ghedda wax, II, 269  
Indian and Chinese beeswax, II, 269  
and **MEISENHEIMER.** Lactic acid, estimation of, VII, 437, 440  
formation of, in wine, VII, 430
- RAPP.** Enzyme in yeast, I, 209

- BUCHNER, E. Fermenting enzyme, zymase, in yeast, I, 213, 214  
Glycogen-splitting enzyme in yeast, I, 212
- BUCKLEY. Tests for helindone, V, 534
- BUCKMASTER. Guaiacum test for blood, VIII, 523  
Malachite green test for blood, VIII, 525  
and GARDNER. Detection of traces of carbon monoxide in blood, VIII, 533
- BUCKMASTER, G. A. See *J. A. Gardner*.
- BUCKNER, W. A. Asafetida, IV, 94
- BUDAI, K. Trimethylamine and ammonia, estimation of, IX, 469
- BUDDE. Rubber, acetone extraction of, IV, 125  
estimation of, IX, 32  
pure, estimation of, in raw rubber, IV, 110  
vulcanisation of, IV, 115  
vulcanised, estimation of sulphur in, IV, 140  
and SCHON. Use of fuming sulphuric acid in the Kjeldahl analysis of refractory substances, VIII, 49
- BUEB. Preparation of cyanides, VII, 474
- BUGLIA. Electrical conductivity of homogenised milk, VIII, 221
- BUIGNET. See *Peligo*.
- BUISINE. Beeswax, effect of bleaching on the constants of, II, 245  
paraffin hydrocarbons in, II, 243  
See *Duvillier*.
- BUISINE, A. and P. Estimation of the hydrocarbons in beeswax, II, 258, 259, 260
- BUJARD, A. Estimation of glycogen in flesh, VIII, 282  
See *Klinger*.
- BUKOWSKY. Phytosterol from oil of lycopodium seeds, II, 485
- BULL. Cod liver oil, composition of, II, 215  
Fish-liver oils, II, 221, 223  
Herring oil, II, 226  
Porpoise oils, II, 231  
Sardine oils, II, 225  
Seal oil, II, 226, 227  
Sperm oil, fatty acids from, II, 235  
iodine value for, II, 240  
Whale oils, II, 228, 229
- BULLE. See *Hayduck*.
- BULL IMPERIAL INSTITUTE. Copals, IX, 310  
Myrrh, IX, 319  
Petitgrain oil, IX, 369  
Thyme oil, IX, 377
- BULLNHEIMER and SEITZ. Composition of Fehling's solution, I, 318
- BUNGE and SCHMIEDEBERG. Estimation of hippuric acid in urine, VII, 394
- BUNGENER, A. See *Lintner*.
- BUNGENER, H. Hop-bitter  $\beta$ -acid, VII, 165
- BUNTZEN and MADSEN. Commercial aconitine, VI, 287
- BUNZEL. Oxydases, measurement of, IX, 591
- BURELL, G. A. and ROBERTSON, J. W. Separation of hydrocarbons, IX, 230
- BURGESS. Apparatus for the exhaustion of organised tissues by solvents, I, 78  
Cinnamic aldehyde, estimation of, III, 441  
Essential oils, estimation of aldehydes and ketones in, IV, 232
- BURGESS and CHILD. Citral, estimation of, IV, 276  
Lemon oil, IV, 352, 354, 355  
estimation of aldehydes in, IV, 274  
Terpeneless lemon oils, IV, 430
- BURGESS, H. E. Test for citronellal, IV, 270  
Test for linalol, IV, 262
- BURIAN. Phytosterols from wheat germs, II, 486, 487  
Sitosterol in wheat oil, II, 148
- BÜRGER. Spectrum of hæmoglobin, VIII, 521
- BURMANN. Alkaloids, detection and estimation of, IX, 479  
Digitalis glucosides, estimation of, VII, 120
- BURMANN, J. Estimation of caffeine in coffee, VI, 609
- BURMEISTER. See *Schenk*.
- BURNETT and REVIS. Polenske value for margarine, IX, 171  
See also *Revis*.
- BURNETT, J. F. Test for alkaloids, VI, 381
- BUROW. Composition of casein, VIII, 121
- BURR. Dried milks, analyses of, VIII, 238  
Acid and rennet curds, analyses of, VIII, 196  
and BERBERICH. Milk sugar, analyses of raw, VIII, 198  
detection of sucrose in, VIII, 202
- BURROWS. See *Tilden*.
- BURSCHELL. Estimation of cyanogen in spent gas purifying mass, VII, 520
- BURSTYN. Estimation of the free acid in olive oil, II, 110
- BURTON, W. M. Estimation of mineral oil in turpentine, IV, 417  
See *Remsen*.
- BURWELL. See *Woodman*.
- BUSCH, A. Manufacture of santonin, VII, 153
- BUSCH, M. Methoxyl number of essential oils, IV, 241  
and BLUME, G. Estimation of picric acid, V, 123
- BUSCH AND CO. Orange oils, IV, 360
- BUSSCHER. Poisoning by aconite, VI, 284
- BUSSE. Pembe cheese, VIII, 241
- BUSSE, W. Black pepper, detection of shells in, VII, 62  
Vanilla, percentage of vanillin in, III, 514
- BUTTENBERG and GUTH. Analysis of Camembert cheese, VIII, 252  
and KOENIG. Analysis of Kräuter Käse, VIII, 253
- BUTTERFIELD. Spectrophotometer constants for oxyhæmoglobin, VIII, 521
- BYASSON. Analysis of maté, VI, 642
- BYWATERS. Nucleoprotein of serum, VIII, 92

## C

- CABOT. Wood-preserving oils, value of higher phenols in, IX, 271
- CADDY. See *Kanthack*.
- CADET. Roasting of coffee, VI, 649
- CAESAR and LORETZ. Aconite, assay of, VI, 281  
Ipecacuanha, percentage of alkaloids in, VII, 48

- CAESAR and LORETZ. Peruvian balsam, detection of artificial, III, 458  
 Strophanthus glucoside, assay of, VII, 122
- CAHOUS. Benzoyl chloride, preparation of, III, 417  
 Methyl salicylate in wintergreen oil, III, 493  
 Salicylic acid, preparation of, III, 466
- CAILLOT. See *Caseneuve*.
- CAIN, J. C. Estimation of ethyl alcohol by the ebullioscopic method, IX, 4  
 and THORPE, J. F. Preparation of magenta, V, 247
- CAINES. See *Squire*.
- CAINES, C. M. Caffeine, estimation of, in tea, VI, 607  
 Coffee parchment, analysis of, VI, 643  
 Tannin, estimation of, in tea, VI, 619
- CAINES, C. H. Analyses of tea, VI, 602
- CALDWELL. Apparatus for the estimation of moisture, ether extract and crude fibre, I, 66  
 Reichert value for oils and fats, II, 23
- CALDWELL, R. J. and WHYMPER. Production of sodium flame, I, 43
- CALTINI. Detection of salicylic acid, IX, 301
- CALVI and MALACARNE. Stability of hydrocyanic acid in corpses, VII, 467
- CAMBE. See *Astruc*.
- CAMBI. Acetone, Legal's test for, IX, 577
- CAMBON. Determination of the melting point of glue, VIII, 611
- CAMERON. See *Orndorff*.
- CAMILLA and PERTUSI. Saccharin, detection of, IX, 288, 290  
 Xanthine bases, detection of, IX, 525
- CAMPANI and GRIMALDI. Lupine alkaloids, VI, 225
- CAMPBELL. See *Graham, Osborne*.
- CAMPBELL, F. H. Moisture in tea, IX, 529
- CAMPBELL-BROWN, J. Long pepper, VII, 65  
 Poivrette, VII, 68
- CAMPION. See *Ranwez*.
- CAMUS. French oil of peppermint, IX, 371  
 Hordenine, physiological properties of, VII, 37
- CANET and DURIEUX. Polarimetric estimation of starch, I, 424
- CANTOR. See *Benedikt*.
- CANZONERI, F. and BIANCHINI, G. Olive oils, IX, 133  
 and PERCIABOSCO. Sesame oil, II, 142
- CAPALDI. Kynurenic acid, estimation of, IX, 569
- CARLES. Caramel, detection of, in wines by the white-of-egg test, I, 179  
 Morphine, estimation of, IX, 505
- CARLES, P. Examination of commercial egg albumin, VIII, 433
- CARLETTI. Abrastol, detection of, III, 402  
 Phenol, detection of, in salicylic acid, III, 471
- CARLINFANTI and LEVI-MALVANO. Eutectic mixtures in fatty acids, II, 387  
 and MARZOCCLIE. Estimation of saccharin, IX, 291
- CARLSON. Guaiacum test for blood, VIII, 523
- CARNELUTTI and VALENTE. Preparation of urine for examination with Fehling solution, I, 396
- CARO. See *Frank*.
- CARON and RAQUET. Assay of bismuth salicylate, IX, 304
- CARPENÉ, A. Estimation of tannin in wine, v, 88
- CARPENTER, W. LANT. Palmitic acid, preparation of, from oleic acid, II, 404  
 Soap, analyses of, II, 444  
 classification of, II, 417
- CARPENTIERI. See *Sostegni*.
- CARR, FRANCIS H. Aconite alkaloids, VI, 253; IX, 487  
 Atropine and its allies, VI, 289; IX, 490  
 Tropeines, detection of, IX, 491  
 and scopoleines, VI, 289  
 See *Barger, Dunstan*.
- and OSBORNE. Estimation of moisture, I, 67
- PYMAN. Ipecacuanha alkaloids, IX, 542  
 constitution of, IX, 544
- REYNOLDS. Alkaloids, rotatory power of, IX, 478  
 Belladonna, alkaloids in, VI, 313  
 Calabar beans, alkaloidal content of, VII, 28  
 Colchicine, percentage of, in colchicum seeds, VII, 10  
 Hyoscyamine, rotation of, VI, 297  
 Hyoscyamus, alkaloid in, VI, 317  
 Ipecacuanha, percentage of alkaloids in, VII, 48  
 Noratropine, IX, 490  
 Norhyoscyamine, IX, 490, 491  
 Pilocarpine, percentage of, in jaborandi, VII, 54  
 Pomegranate bark, assay of, VII, 50  
 Sparteine, percentage of, in broom, VII, 68
- CARTEL. Analysis of French mustard, VII, 115
- CARTER. See *Gardner*.
- CARTIER. Hydrometer of, I, 15
- CASAGRANDE. Cell wall of yeast, I, 206  
 See *Will*.
- CASALI. Estimation of free sulphuric acid in vinegar, I, 503
- CASALI, A. Estimation of tannins, v, 90
- CASAMAJOR. Detection of starch-sugar as an adulterant of cane sugar, I, 355
- CASH and DUNSTAN. Aconite bases, pharmacology of, VI, 287  
 Indaconitine, physiological action of, VI, 269
- CASPARI. Codeine, estimation of, VI, 394  
 Gutta-percha, action of nitrous anhydride on, IV, 157  
 India-rubber, analysis of, IX, 322  
 estimation of, IX, 321  
 properties of, IV, 110
- CASPARI, C. B. Santonin, estimation of, in wormseed, IX, 550
- CAUSSE. Estimation of phenylhydrazine, VI, 34
- CAZENEUVE, M. P. Constitution of pseudomorphine, VI, 357  
 and BRETEAU. Solanine and colchicine, reaction of strong nitric acid with, VI, 200  
 formula for, VII, 90



- CAZENEUVE and BRETEAU. Solanine and colchicine, preparation of, from potato, VII, 89
- CAILLOT. Percentage of piperine in Sumatra pepper, VII, 55
- LÉPINE. Poisoning by Martin's yellow, v, 126
- CECCHERELLI. Estimation of saccharin, IX, 291
- CEDERCREUTZ. See *Lunge*.
- CEDIVODA. See *Dits*.
- CHABOT, P. Specific rotation of camphor, IV, 195
- CHACE. Citral, estimation of, IX, 337  
Saccharin, detection of, in foods and beverages, III, 432
- CHACE, E. M. Detection of pinene in lemon oil, IV, 356
- CHAMBERLAIN. Estimation of gliadin in flour, VIII, 101
- CHAMBERLAND. Filter, VIII, 118
- CHAMOT. Determination of the nature of the base in soap grease, III, 178
- CHANCE, EDWIN M. Technical examination of creosote oils, III, 377
- CHANCEL. Specific gravity of solutions of invert sugar, I, 289
- CHANDLER, C. F. Scales in use for Baumé's hydrometers, I, 8
- CHAPIN, HENRY D. Use of hydrogen peroxide as a preservative, VIII, 690  
and POWICK. Estimation of phosphorus in meat and eggs, IX, 611
- CHAPMAN. Chinese wood oil, IX, 141, 142  
Jaffé reaction for creatinine, VIII, 411  
Japanese wood oil, IX, 144  
Picrate reaction for hydrogen cyanide, VII, 470  
See *Welch*.  
and ROLFE. Blown oils, II, 362  
SMITH. Determination of the structure of isomeric bodies, I, 236  
Examination of esters, I, 236  
WHITTERIDGE. Estimation of tartaric acid, IX, 104
- CHAPMAN, A. C. Allyl- and propenyl-phenols, colour reactions for detecting, IV, 299  
Hop oil, IX, 383  
Hops, antiseptic power of, IX, 553  
arsenic in, IX, 559  
determination of resins in, IX, 557  
essential oil in, VII, 173  
estimation of tannin in, v, 91; VII, 187, 188  
nitrogenous constituents of, IX, 550, 551  
and quassia in beer, method for distinguishing between, I, 161  
 $\gamma$ -resin from, VII, 167  
valuation of, VII, 174  
Humulene, IX, 363  
Tea, estimation of tannin in, v, 91  
Zinc, use of, in the estimation of arsenic in malt, I, 146
- CHARABOT. Lavender oil, IX, 365  
Linalol in bergamot oil, IV, 317  
Terpenes, formation of, during the development of plants, IV, 220
- CHARABOT, E. Menthol, IV, 282
- CHARAUX. Estimation of chlorogenic acid, VI, 646
- CHARITSCHKOFF. Separation of hydrocarbons, IX, 230
- CHARNASS. See *Färth*.
- CHARTERIS, M. Cresotic acid, effect of the presence of, in artificial salicylic acid, III, 472  
physiological action of, III, 509
- CHASTAING. Phenoloid character of morphine, VI, 376
- CHATEAU. Solidification of linseed oil, II, 331
- CHATTAWAY, W. Beeswax, specific gravity of, II, 250  
Glycerol test for wood-creosote, III, 360  
Wool-fat, examination of, II, 496, 497  
and MOOR. Standard of ash in colocynth pulp, VII, 160  
PEARMAN and MOOR. Modification of the Valenta test for fats and oils, II, 62
- CHAUVIN. Detection of vanillin, IX, 307
- CHEMISCHE FABRIK GRIESHEIM-ELEKTRO. Thioxine blacks, v, 378  
yellow G, orange, v, 376
- CHÉNEAU, O. Analysis of vulcanised rubber, IV, 142
- CHERCHEFFSKY, N. Ceresin and paraffin, separation of, IX, 257  
Glue, determination of the melting point of, VIII, 610
- CHEMNORUKII, H. Caviare, IX, 622
- CHESTER, A. H. Meat-extracts, VIII, 396
- CHEVALIER. Alkaloids in belladonna, effect of manures on the percentage of, VI, 313  
yield of, in plants, VI, 170  
Broom, percentage of sparteine in, VII, 68  
See *Goris*, *Payen*.  
and PELLETAN. Berberine, VI, 551
- CHEVASTELON. Estimation of acetylene, III, 9
- CHEVREUL. Linseed oil, effect of temperature and storage on the drying of, II, 349  
Sperm oil, composition of, II, 233  
Valeric acid from porpoise oil, II, 230  
See *Ramsay*.
- CHICK and MARTIN. Coagulation, VIII, 54
- CHICK, OLIVER. Cinchona alkaloids, VI, 479; IX, 514  
See *B. F. Howard*.
- CHILD. See *Burgess*.
- CHITTENDEN. See *Kühne*.  
and HARTWELL. Analysis of elastin, VIII, 631  
SMITH. Palmitates, influence of acetic acid on the solubility of, in alcohol, II, 396  
Palmitic acid, preparation of, II, 395  
Palmitins, II, 397  
SOLLEY. Products of the digestion of gelatin, VIII, 597
- CHOAY. See *Béhal*.
- CHODAT. Oxydases, vegetable, IX, 591
- CHRÉTIEN. Recovery of tertiary amines from their acid ferrocyanides, VI, 10
- CHRISTISON. Commercial gamboge, v, 417
- CHRISTOMANOS. Determination of the melting points of fats by the formation of an electric circuit, II, 54



- CHRISTY.** Estimation of gold in cyanide solutions, VII, 494
- CHURCH.** Cocoa nibs, analysis of, VI, 689  
Exhauster for the estimation of oils and fats, II, 5  
Linseed oil, composition of, II, 330  
percentage of, in linseed, II, 324  
Vegetable products, analyses of, I, 451
- CHURCH, A. H.** Cyclopic acid, VI, 602  
Mutton-chops, composition of, VIII, 263  
Turacin, VIII, 559
- CHWOLLES.** Phloroglucinol test for almond-kernel and peach-kernel oils, II, 104  
applied to almond oil, III, 422
- CIAMICIAN and RAVENNA.** Tobacco, alkaloids in, IX, 477
- SILBER.** Alkaloids, nomenclature of, VI, 170  
Angelica oil, crystalline substances from, IV, 310  
Cinnamon oil, constituents of, IX, 357  
Curcumin, formula for, V, 414  
Pseudo-pelletierine, VI, 231
- CLAASSEN.** Estimation of codeine, VI, 393
- CLAPLIN.** Preparation of lactic acid from sugar, VII, 430
- CLAPP.** Wheat proteins, VIII, 97  
See *Osborne*.
- CLARK, J.** Percentage of sand in snuff, VI, 250
- CLARK, W. INGLIS.** Determination of the proportion of ethyl acetate in the commercial liquid, I, 238  
See *Allbright, Sherman*.
- CLARKE and HURTLEY.** Sulphæmoglobin, VIII, 539
- CLAUS and WILGERODT.** Melting point of alizarin, V, 207
- CLAUSER.** See *Dils*.
- CLAUSNIZER.** Effect of the addition of lime to glycerol, II, 457  
and **MAYER.** Calculations for the analysis of milk, VIII, 163
- CLAYTON, E. G.** Caffeine in coffee infusions, VI, 680  
Cocoa essences, analyses of, VI, 693  
Glue, estimation of the non-gelatinous substances in, VIII, 612  
examination of, VIII, 603
- CLEAVER, E. L.** Action of solvents on opium, VI, 415
- CLEMANTI.** Arginine, IX, 625
- CLENNELL, J. E.** Cyanide, commercial, estimation of the hydroxides in, VII, 485  
solutions, estimation of the solvent activity of, VII, 495
- CLEWER.** See *Tulin*.
- CLÖRZ.** Linseed oil, composition of, II, 329  
and poppy oils, change in composition of, by exposure to air, II, 345  
Tung oil, composition of, II, 155
- CLOTWORTHY.** See *Thompson*.
- CLOVER.** See *Harris*.
- CLOWES, F.** Oxidation of pyrogallol, III, 537
- CLOWES, G. H. A.** Indicators, III, 552
- CLUBE, D.** See *A. J. Brown*.
- COBLENTZ, VIRGIL.** Wood-tar creosote, III, 347
- COBURN.** See *Hopkins*.
- COCHENHAUSEN.** Estimation of free fatty acids in wool-fat, II, 499
- COCHRAN.** Analysis of milk, VIII, 142
- COCHRAN, C. B.** Inversion of sugar in sweetened condensed milk, I, 371
- COCKBURN, T. and BLACK, J. W.** Estimation of quinine, IX, 516
- COCKING.** Detection of African copaiba, IX, 313  
See *Hill*.  
and **KETTLE.** Estimation of balsamic acids, IX, 294
- COFFIGNIER.** Copals, IV, 56  
Dammar resin, IX, 310  
Manila copal, IV, 52  
Prussian blue, solubility of, in hydrochloric acid and alcohol, VII, 507
- COHEN.** See *Ministi*.
- COHN.** Beeswax, determination of the saponification value of, II, 253  
Lecithin, estimation of, in eggs, IX, 620
- COLBY.** Iodine value for olive oil, II, 113, 114
- COLE.** Estimation of lactose, IX, 57  
See *Hopkins*.
- COLIN.** Artificial silk, VIII, 670
- COLLARD.** Opium, estimation of morphine in, IX, 504
- COLLIE, J. N.** See *W. Garsel*.
- COLLIER, H.** Resin soaps, IV, 32
- COLLIN.** Mustard, adulteration of, VII, 112  
Pepper and its adulterants, microscopical examination of, VII, 59  
See also *Villiers*.  
and **BENOIST.** Estimation of tannin, V, 86
- COLLINGRIDGE.** See *Ramsay*.
- COLLINS.** Evolution of hydrocyanic acid from linseed cake, IX, 183
- COLMAN.** Hair-dye, VIII, 680  
and **SMITH.** Naphthalene, estimation of, in coal gas, III, 245, 246
- COLMAN, H. G.** Estimation of toluene in commercial coal-tar distillates, IX, 230
- COLOMBANO.** See *Oddo*.
- COMANDUCCI, EZIO.** Cinchona alkaloids, constitution of, VI, 503  
Quinine, estimation of, VI, 511  
Saccharin, detection of, IX, 290
- COMBEMALE.** See *Mairel*.
- COMBY.** See *Jackson*.
- COMMAILLE, A.** Caffeine, solubility of, VI, 583  
Coffee, composition of, VI, 644
- CONDELLI.** Estimation of saccharin, IX, 291
- CONE.** See *Gomberg*.
- CONGDON.** Condensed soups, IX, 618
- DE CONINCK.** Pyridine bases, test for, VI, 129
- DE CONINCK, O.** Base from putrid cuttle fish, VII, 353  
Reactions of substituted anilines, VI, 91
- DE CONINCK, W. O.** Distinction between succinic and malic acids, IX, 99
- CONNSTEIN, HOYER and WARTENBERG.** Hydrolysis of fats by lipoclastic enzymes, II, 11
- CONRADSON.** Lubricating greases, determination of the water in, III, 179  
oils, carbon test for, IX, 250

- CONRADSON, P. H. Detection of rosin spirit in turpentine oil, IV, 422
- CONRADY. Terpenes, IV, 166  
See *Tschirch*.
- CONROY. Sodium ferrocyanide, solubility of, VII, 506
- CONROY, M. Opium, assay of, VI, 423, 426  
Rose oil, IV, 386
- CONSTAM. See *Goldschmidt*.
- CONTI. Bouillon cubes, IX, 617
- COOK. Bouillon cubes, IX, 616  
Eggs, changes in, in cold storage, VIII, 444  
weights of, VIII, 439, 441  
Meat and yeast extracts, composition of, VIII, 416, 419  
and plant-extracts, differentiation of, IX, 615  
See *Bigelow*.
- COOKE. See *Gorslin*.
- COOMBS and RUSSELL. Mangrove, IX, 395
- COPEMAN, S. M. Preparation of hæmoglobin, VIII, 508
- COPETTI. See *Guglielmotti*.
- COPPELTI. Test for dyed silks, VIII, 667
- COPTTHORNE. See *Eisenschmil*.
- CORDOSO and BAUME. Critical temperature and pressure of cyanogen, VII, 455  
MASTBAUM. Analyses of Portuguese cheeses, VIII, 251
- COREMONS. See *Cowley*.
- CORNELIO. See *Martinotti*.
- CORNELISON. Detection of colouring matters in butter, V, 665
- CORNELL. See *Harrison*.
- CORNWALL. Detection of annatto and saffron in butter, V, 664
- CORRIDI. Estimation of tannins, V, 95
- CORRIEZ. Sparteine and its salts, IX, 483, 541
- COSTE, J. H. Polymerisation of turpentine, IX, 381  
and SHELBURN. Neatsfoot oil, II, 201  
Nitric acid test for cottonseed oil, II, 139
- COSTES. Extraction of caffeine in coffee, IX, 527
- COTTON. Detection of sucrose in milk, VIII, 166
- COUERBE. Alkaloids of sabadilla, VII, 69  
of stavesacre, VII, 15
- COUNCIL OF THE INSTITUTE OF BREWING. Estimation of malt, I, 134
- COUNCLER, C. Analysis of tannin yielding materials, V, 31  
and VON SCHROEDER. Reduction-equivalent of gallotannic acid, V, 64
- COURANT. Calcium casein, VIII, 124
- COURLAY and COREMONS. Detection of horse flesh in sausages, VIII, 377
- COURT. See *Pictet*.
- COUSIN, H. Action of sulphuric acid on catechol, III, 341
- COUTTS. Analyses of condensed milk, VIII, 212
- COUTY, GUIMARAES and NIOBEY. Effect of coffee as a beverage, VI, 651
- COUX. Artificial silk, VIII, 670
- COWIE, W. B. Tests for jalap resin, VII, 132  
and BRANDER. Mexican scammony resin, VII, 133
- COWNLEY, A. J. Shaefer's and MacLagan's tests for cocaine, VI, 335  
See *Paul*.
- COX, G. S. Imitation of cider-vinegar, I, 497
- CRÄMER. Sericin and fibroin, VIII, 635
- CRAFTS, J. M. Assay of commercial xylenes, III, 217  
See *Friedel*.
- CRAIG, A. G. Estimation of formaldehyde by the ammonia method, I, 262
- CRAMPTON and SIMONS. Caramel, test for, V, 639  
Palm oil, detection of, in butter, II, 310
- TOLMAN. American whisky, I, 202  
Potable spirits, estimation of higher alcohols in, I, 190
- TRESCOT. Absorption apparatus for the determination of carbon dioxide in beer, I, 159
- CRANFIELD. Reichert-Meissel values for butter fat, IX, 152
- CRAWFORD. Estimation of adulteration of cider vinegar, IX, 95  
and DOHME. Pharmacology of narcotine, VI, 401
- CREMER. Enzyme in yeast, I, 209  
Yeast-glycogen, I, 209  
See *Tschirch*.
- CRIBB. Condenser, I, 18
- CRIPPS. Coniine, assay of, in hemlock, VI, 223  
Essential oils, iodine value of, IV, 239  
and BROWN. Estimation of essential oils in spices, IX, 293  
DYMOND. Tests for aloes, VII, 145  
WRIGHT. Flour, estimation of sulphates in, IX, 593
- CRIPPS, R. A. Colchicine, extraction of, VII, 9  
Emetine, percentage composition of, VII, 39  
Ipecacuanha, assay of, VII, 46  
percentage of alkaloids in, VII, 47, 48  
spurious, VII, 49  
and WHITLEY. Ipecacuanha, alkaloids, VII, 40, 48  
reactions of, VII, 42  
assay of, VII, 44
- CRISMER. The critical temperature of solution of fats and oils, II, 63
- CROFT-HILL. Starch, estimation of, IX, 71  
Sugars, estimation of with Pavy's solution, I, 332  
measurement of the hydrolysis of, by enzymes, VIII, 8  
"Yeast-glucose," I, 211
- CROISSANT and BRETONNIÈRE. Sulphur dyes, V, 374
- CRONER and CRONHEIM. Test for lactic acid, VII, 435
- CRONHEIM. See *Croner*.
- CROSS. See *Bevan*.  
and BEVAN. Cellulose, estimation of, I, 436; IX, 78  
Fibres for paper making, examination of, I, 484  
Lustrocellulose, composition of, VIII, 669  
Plant celluloses, classification of, I, 433  
and BRIGGS. Gelatin chloramine, VIII, 591

- CROSS and JENKS.** Sulphuric esters in gun cotton, III, 568  
**TAGGART.** Inversion of saccharose, IX, 47  
**CROSSLEY.** Hydrogenation of oils, IX, 122  
**and LE SUEUR.** Arachis oil, properties of, II, 91, 92  
 Coconut oil, specific gravity of, II, 188  
*Eruca sativa* seed oil, properties of, II, 121  
 Indian mustard oil, properties of, II, 121  
 Olive oil, iodine value for, II, 113  
 specific gravity of, II, 112  
 Poppyseed oil, rotation and viscosity of, II, 153  
 Rape oil, crude, constants for, II, 124, 126  
 specific gravity of, II, 127  
 viscosity of, II, 128  
 Safflower oil, constants for, II, 154  
 Walnut oil, butyro-refractometer value for, II, 158  
**CULLEN.** Abel heat test for explosives, III, 606  
**CUNIASSE.** See *Girard*.  
**CUNNINGHAM and DOREÉ.** Formation of hydroxyfurfuraldehyde from carbohydrates, IX, 64  
**CURTIUS.** Preparation of azoimide, VI, 27  
**and JAY.** Preparation of hydrazine hydrate, VI, 24  
**SCHRADER.** Test for hydrazine, VI, 25  
**SCHULZ.** Preparation of hydrazine hydrate, VI, 24  
**CURTMAN, C. O.** Detection of salicylic acid in wine or beer, III, 478  
**CUSHNY.** Gelsemine, formula for, VII, 32  
*d*-Hyoscyamine, VI, 298  
**CUTTER and GIES.** Chondroproteins, VIII, 91  
**CZUMPELITZ.** Reaction of zinc chloride with alkaloids, VI, 198  
**CZYLHARZ, FUCHS and v. FURTH.** Bile pigments, estimation of, IX, 579  
**and VON FÜRTH.** Oxydase, estimation of, VIII, 14  
 Malachite green test for blood, VIII, 525
- D**
- DACLIN.** Detection of santonin in urine, VII, 156  
**DAHMS, P.** Presence of free succinic acid in amber, IV, 18  
**DAISH, A. J.** Reducing power of xylose and arabinose, IX, 62  
 See *Davis*.  
**DAKIN.** Addition of potassium persulphate in the Kjeldal analysis of refractory substances, VIII, 49  
 Hippuric acid, estimation of, IX, 569  
 See *Kossel*.  
**DALE.** Physiological properties of ergotoxine, VII, 23  
 See *Barger*.  
**and DIXON.** Physiological action of *p*-hydroxyphenylethylamine, VII, 347  
 Physiological action of *iso*-amylamine, VII, 345  
**LAIDLAW.** Methylcytisine, IX, 536  
**DALE and LAIDLAW.** Physiological properties of iminazolyethylamine, VII, 350  
**DALICAN.** Determination of the solidification point of fats and oils, II, 55  
**DALICAN, F.** Assay of tallow for the detection of palm-nut and coconut oils, II, 213  
**VAN DAM.** Ripening of cheese, VIII, 244  
 Testing of rennet, VIII, 131  
**DAMIENS.** See *Lebeau*.  
**DANGEARD, JANSSENS and WAGER.** Nucleus of yeast cell, I, 207  
**DANIELS.** Uric acid, output of, IX, 571  
**DANILEWSKY and RADENHAUSEN.** Caseinogen, VIII, 74, 91  
**DARBY, S.** Fluid meat, VIII, 396  
**DARE.** Hæmoglobinometer, VIII, 564  
**DAREKY and GÉRARD.** Fat content of yeast, I, 209  
**DARMSTÄDTER and LIFSCHÜTZ.** Composition of wool-fat, II, 496  
**DARTON, N. H.** Estimation of tannins, v, 69  
**DAVID.** Berberine, estimation of, IX, 522  
 Hydrastine, estimation of, IX, 524  
**DAVIDSON.** Drying of oil on glass, determination of rate of, IX, 195  
 Flax, cultivation of, IX, 180  
**DAVIES.** Condenser, I, 18  
**and McLELLAN.** Cacao butter, percentage of, in roasted cocoa beans, II, 177  
 Fat, percentage of, in cocoa, VI, 701  
**DAVIES, E.** Asphalts, behaviour of, with petroleum spirit, III, 63  
 Urine after carbolic acid poisoning, III, 400  
**DAVIES, R. H.** Action of mercuric chloride on caffeine, VI, 588  
**DAVIS.** Essential oils, iodine value of, IV, 239, 240  
*d*-Lupanine, VI, 228  
 See *Schmidt, Woodman*.  
**DAVIS, G. E.** Assay of crude coal-tar naphthas, III, 236  
**and T. H.** Anthraquinone test for anthracene, III, 282  
**DAVIS, W. A.** Amines and ammonium bases, VI, I; IX, 469  
 Glycerol, II, 447; IX, 211  
 Lactic acid, VII, 429; IX, 582  
 Lead, assay of, in tartar, I, 549  
 detection of, I, 568  
 Maltose, hydrolysis of, IX, 48  
 Naphthalene and its derivatives, III, 243; IX, 266  
 $\alpha$ - and  $\beta$ -naphthol, bromo-compounds of, I, 253  
 Naphthols, etherification of the, III, 253  
 Organic analysis, introduction to, I, I  
 Perchloric acid, use of, in the separation of potassium and sodium in canned meat, VIII, 335  
 Phthalic acid and the phthaleins, III, 541  
 Starch and its isomerides, IX, 70  
 Starch, action of enzymes on, IX, 77  
 estimation of, by taka-diastase, IX, 73  
 Sugar analysis, IX, 50, 51  
 Sugars, IX, 19, 625  
 See *Thomas, Arthur W., Dreaper*.

- DAVIS, W. A. and DAISH. Maltose, estimation of, IX, 53  
 Plant extracts, analysis of, IX, 46, 48, 63, 64  
 Starch, action of acids on, IX, 77  
 estimation of, IX, 70  
 Sugars, estimation of, IX, 22  
 solution densities of, IX, 19  
 KLEIN. Extraction of linseed oil from paint, II, 329  
 SAWYER. Maltose, estimation of, IX, 54  
 Pentoses in plant extracts, IX, 63  
 DAVIS, W. C. Estimation of naphthalene in spent oxide, IX, 268  
 DAVOLL. Estimation of sugar in beet, I, 361  
 DAVY. Precipitation of gelatin with platinic sulphate, VIII, 591  
 DAVY, H. (SIR). Estimation of tannins, v, 85  
 DAY. Asphalt, composition of, III, 63  
 Gilsonite, estimation of sulphur in, III, 84  
 See *Baker*.  
 and GILPIN. Fuller's earth test for petroleums, III, 48  
 DEAN. Coumarin, detection of, in vanilla, IX, 306  
 Creosote oil, estimation of the volatility of, III, 379  
 Lubricating greases, determination of the water in, III, 180  
 and BATEMAN. Creosote oil, specifications for, III, 369  
 Sulphonation test, III, 28  
 DEAN, A. L. and DOWNS, C. R. Wood-preserving oils, antiseptic tests of, IX, 276  
 DEBOURDEAUX. Opium, estimation of morphine in, IX, 504, 507  
 DECKER. See *Kropp*.  
 DEELEY. See *Archbutt*.  
 VAN DEEN. Gualacum test for blood, VIII, 523  
 DEERING. Free oleic acid in tallow, II, 209  
 and REDWOOD. Castor oil, rotation of, II, 159, 160  
 solubility of, in alcohol, II, 162  
 viscosity of, II, 162  
 DEFERT. Potassium in coffee ash, VI, 654  
 DEFRESNE, T. Estimation of peptones, VIII, 396  
 DEFRIS. See *Ulser*.  
 DEGRAZIA. Estimation of nicotine, IX, 486  
 DEILER, A. C. and TRAPS, G. S. Walnut oil, IX, 145  
 DEITER. See *Beythien*.  
 DEKKER, J. Cocoa, estimation of theobromine and caffeine in, VI, 709  
 husks, VI, 696  
 Theobromine in kola leaves, VI, 682  
 Tannin materials, IX, 384  
 DEKONINCK, L. L. and JOASTART, N. Ferrocyanides, estimation of, IX, 588  
 DELAGE, M. Sulphonic acids of pyrogallol, III, 538  
 DELBRÜCK. Odour of yeast, IX, 15  
 DELEARDE and BENOIT, A. Phenolphthalein test for blood, VIII, 525  
 DELÉPINE. Separation of amines, VI, 7  
 and SORNET. Pyridine, estimation of, IX, 475  
 DELÉPINE, S. Calcium urate in gouty deposits, VII, 379  
 DELHAYE. See *Etienne*.  
 DELLE. Detection of saccharin in foods and beverages, III, 433  
 DELONDRE. See *Soubeyran*.  
 DELPHIN. Analysis of Tolu balsam, III, 460  
 DELVILDE, M. P. Origin of bitumens, III, 37  
 DEMME. Physiological action of creosotic acids, III, 509  
 DEMSKI and MORAWSKI. Detection and estimation of rosin oil in mineral oil, IV, 45  
 DENAEYER, A. Peptones, analysis of, VIII, 396  
 value of, VIII, 397  
 DENIGES. Acetone, estimation of, I, 107  
 Benzene, estimation of thiophen in, III, 211  
 Benzoic acid, detection of, IX, 280  
 Benzoyl group, colour reaction for the detection of the, III, 403  
 Citric acid, estimation of, IX, 112  
 Essential oils, detection of ethyl citrate in, IX, 331  
 Lactic acid, detection of, VII, 434  
 Methyl alcohol, detection and estimation of, in the presence of ethyl alcohol, IX, 1  
 Milk, estimation of citrates in, VIII, 161, 162  
 Morphine, estimation of, VI, 386  
 Wood naphtha, estimation of acetone and higher ketones in, I, 100  
 DÉNIS. Separation of proteins by precipitation with salts, VIII, 64  
 DÉNIS, W. See *O. Folin*.  
 and DUNBAR. Almond flavouring extracts, analysis of, III, 419  
 Benzaldehyde, estimation of, IX, 286  
 DENNSTEDT. Estimation of carbon and hydrogen by combustion, I, 57  
 DENTON. See *Gardner*.  
 DESGREZ and NICLOUX. Detection of carbon monoxide in blood, VIII, 535  
 DESMOULIÈRE. Gelatin, detection of, in preserves, VIII, 593  
 Milk. Estimation of citrates in, VIII, 160  
 See *Porter*.  
 DEUSSEN, E. Estimation of camphor in spirits of camphor, IV, 200  
 and EGER. Oil of copaiba, IX, 314  
 DEWAR. Formation of hydrocyanic acid in the electric arc, VII, 462  
 DEY, KANNY LALL. Indian opium, porphyroxine in, VI, 410  
 test for, VI, 403  
 DHÉRE. Hæmocyanin, VIII, 559  
 DICK. See *Baker*.  
 DICKINSON. See *Langley*.  
 DIECKHOFF. See *Engler*.  
 DIEDRICH. See *Sprinkmeyer*.  
 DIELS and ABDERHALDEN. Cholesterione, formation of, from cholesterol, II, 482  
 Cholesteryl chloride, preparation of, II, 481  
 DIETERICH. Almond oil, detection of peach-kernel and apricot-kernel oil in, II, 104  
 Beeswax, analysis of, from combs five years old, II, 262

- DIETERICH.** Beeswax, effect of bleaching on the constants of, II, 245, 246  
solubility of, in chloroform, II, 243  
Catechu and gambier, distinction between, v, 34  
Colophony, determination of the acid value of, IV, 25  
Elemi, constants for, IV, 96  
Gambier, detection of, v, 104  
Linseed oil, melting point of the fatty acids from, II, 350  
Mustard, analyses of, VII, 107  
Rosolic acid, use of, in the estimation of alkaloids, VI, 182  
Tannins, test for, IX, 403
- DIETERICH, E.** Ammoniacum, varieties of, IV, 92  
Amine resin, IV, 57  
Galbanum, constants for, IV, 97  
Gum-resin from asafotida, IV, 95  
Myrrh, IV, 100  
Sandarac, IV, 58  
Storax, crude, analysis of, III, 463  
Turpentine, constants for, IV, 76  
Venice turpentine, constants for, IV, 77
- DIETERICH, E. and K.** Constants for resins, IV, 10, 13
- DIETERICH, J.** Aloes, detection of, in animal matters, VII, 151
- DIETERICH, K.** Asafotida, IV, 94, 95  
Benzoin, analysis of, III, 451, 456  
Dammar resin, acid value of, IV, 62  
Dragon's blood resin, IV, 62, 63, 64  
Guaiacum, IV, 66  
Myrrh, IV, 100, 101  
Peruvian balsam, adulterations of, IX, 296, 297  
Resins, examination of, IV, 9, 10  
Sandarac, IV, 58  
Shellac and colophony, mixtures of, IV, 73  
Storax, liquid, analysis of, III, 462  
Tolu balsam, detection of, in Peruvian balsam, III, 458  
Turpentine, constants for, IV, 76, 78  
Venice turpentine, constants for, IV, 77, 78  
See *Tschirch*.
- DIETZ.** Synthetic action of lipase
- DIETZE.** Constants for French turpentine, IV, 76
- DIETZE, F.** Acid and ester numbers of rose oil, IV, 387
- DIEUDONNÉ, H.** Estimation of tannins, v, 85
- DILLING.** Coniine, VI, 212  
alkaloids, differentiation of, VI, 221  
tests for, VI, 217
- DILLING, W. J.** Preparation of hæmochromogen, VIII, 549
- DINSLAGE.** Caviare, IX, 622
- DIRCKS, U.** Composition of black mustard seed, VII, 108
- DITMAR.** India-rubber latex, analysis of, IV, 106  
Resins in india-rubber, IV, 108  
Vulcanised rubber, analysis of, IV, 119
- DITTMAR and FAWSITT.** Specific gravity of methyl alcohol, I, 86
- DITTRICH.** Spectrum of methæmoglobin, VIII, 690
- DITZ, H.** Estimation of *m*-cresol in a mixture of cresols, III, 314  
and **CEDIVODA.** Bromo-derivatives of *o*- and *p*-cresol, III, 312
- CLAUSER.** Analysis of disinfectants, III, 333
- DIVERS.** Formula of fulminic acid, VII, 542
- DIXON.** Formation of carbon monoxide and nitrogen by the explosion of cyanogen and oxygen, VII, 455  
See *Dale*.  
and **TAYLOR.** Physiological action of *p*-hydroxyphenylethylamine, VII, 347
- DOBB.** Rise of temperature on the addition of sulphuric acid to fixed oils, II, 59
- DOBBIE.** Constitution of cotarnine, VI, 358  
and **FOX.** Constitution of cinchona alkaloids, IX, 515
- LAUDER.** Absorption spectra of hydrastinine, VI, 572  
Absorption spectra of oxynarcotine and gnoscopine, VI, 361  
Corydaline, oxidation of, VI, 205
- DOBRINER.** Detection of hexamethylene tetramine in medicines, I, 263
- DOBSON and PERKIN.** Xanthaline, VI, 407
- DODD.** See *Smethek*.
- DODGE.** Alcohol in rose oil, IV, 383  
Benzaldehyde, estimation of, IX, 286  
Cineol, estimation of, in eucalyptus oil, IX, 359  
Tannin, estimation of, v, 88
- DODGE, F. E.** Coal-tar pitch tests, III, 30
- DOEBERLINER.** Bitter substance from hops, VII, 169
- DÖBNER.** Synthetic resins, IV, 64  
and **LÜCKER.** Guaiacic and guaiaconic acids, IV, 5  
Guaiacum, IV, 64
- DOEBNER.** Citronellal and citral, separation of, IV, 273  
constitution of, IV, 269  
Resins, composition of, IV, 1
- DOERPMANN.** Morphine, toxicology of, IX, 508
- DÖRPINGHANS.** See *Fischer*.
- DOHERTY.** Estimation of vanillin, IX, 308
- DOHME.** Aconite, assay of, VI, 281, 282  
Morphine, estimation of, IX, 506  
Opium, alkaloids in, VI, 409  
assay of, VI, 422, 426  
See *Crawford*.
- DOHRN.** See *Nicolaier*.
- DOLENCOURT.** Sparteine, IX, 483
- DOMBROWSKI.** See *Bondsinski*.
- DOMERGUE, A.** Analyses of coffee extracts, VI, 678
- DOMMERGUE, G.** Colouring matters from meat products, detection of, VIII, 383  
Colouring matters on wool, examination of, v, 486, 510, 512
- DONATH.** See *Weiser*.  
and **MARGOSCHES.** Estimation of ferrocyanides in the presence of other iron, VII, 492
- MAYRHOFER.** Estimation of sugar in soap, II, 434
- STRASSER.** Estimation of indigotin, v, 395

- DONK.** See *Veitch*.
- DONOGANY.** Test for blood stains, VIII, 576
- DONS.** Butter, refractive index of the fatty acids from, II, 283  
coconut-oil, detection of, in butter fat, II, 284
- DOOLITTLE.** Distinction between annatto and coal-tar colours in butter, II, 308
- DOOLITTLE, O. S.** Torsion viscosimeter for lubricating oils, III, 154
- DOOLITTLE, R. E. and WOODRUFF, F. O.** Estimation of the extract from tea, VI, 622
- DORAN.** See *Adams*.
- DORÉ.** Cholesterol, occurrence of, in sea anemones, II, 479  
Phytosterol from *cliona ciliata*, II, 486  
See *Cunningham*.
- DOREMUS.** Apparatus for the collection of gases from canned meat, VIII, 332
- DORMANN.** See *Piloty*.
- DORMEYER.** Fat, extraction of, from animal organs and tissues, II, 489; IX, 223  
Hydrastine, VI, 564
- DOROGI.** See *Willstätter*.
- DOTT, D. B.** Apocodeine, VI, 395  
Apomorphine, formation of, in solutions of morphine hydrochloride, VI, 388  
hydrochloride, VI, 388  
Bismuth salicylate, commercial, III, 490  
Cineol, estimation of, in eucalyptus oils, IV, 339  
Ethyl-morphine, solubility of, IX, 500  
Morphine hydrochloride, solubility of, VI, 377  
test for, VI, 379  
Morphine-narcotine meconate, assay of, IX, 503  
Narceine, melting point of, VI, 399  
Narcotine, constitution of, VI, 358  
salts of, VI, 401  
Opium alkaloids, separation of, VI, 372  
assay of, VI, 416, 421, 424  
Strychnine, test for brucine in, IX, 510
- DOWNES, C. R.** See *A. L. Dean*.
- DOWZARD.** Anise oils, rotation of, IV, 313  
Benzoin, assay of tincture of, III, 453  
Castor oil, rotation of, II, 160  
solubility of, in absolute alcohol, II, 162  
Codliver oil, refraction of, II, 217  
Colocynth pulp, standard of oil in, VII, 160  
Essential oils, solubility value of, IV, 248  
Opium, assay of, VI, 425, 426  
Oregon balsam, IV, 79  
Saffron, testing of, V, 420
- DRAGENDORFF.** Abietic acid, melting point of, IV, 22  
Alphol and betol, distinction between, III, 499  
Benzoyl guaiacol, reactions of, III, 416  
Essential oils, detection of alcohol in, IV, 246  
solubility of, in water, IV, 221  
See *Zinoffski*.
- and **SPOHN.** *Aconitum vulparia*, extraction of the bases of, VI, 273  
Myoctonine, VI, 275
- REAPER, W. P.** Dyestuffs, estimation of, V, 480; IX, 419  
Fibroids, VIII, 631; IX, 623  
Gallic acid and its allies, III, 525  
estimation of, III, 531, 533  
and tannic acids, separation of, III, 529  
Leather, analysis of, V, 105; IX, 411  
Silk, artificial, VIII, 670  
and artificial silk fibres, strength of, VIII, 664  
test for, VIII, 647  
Tannins, V, 1; IX, 384  
estimation of, V, 59, 70, 90  
See *R. T. May, Williams*.
- and **DAVIS.** Strength of silk and artificial silk fibres, VIII, 664
- FEILMANN, E.** Colouring matters, V, 115  
analysis of, V, 435
- WILSON.** Tannins, estimation of, V, 59  
Gallic acid, precipitation of, by albumin, III, 529
- DRECHSEL.** Exhauster for the estimation of oils and fats, II, 5  
Urea, action of heat on, VII, 390
- DREGER, W.** Formation of tetrabromodiphenylamine, VI, 96
- DREHER.** Lactolin, VII, 447  
Titanic and lactic acids, compounds of, used in the leather industry, VII, 448
- DREHSCHMIDT.** Cyanogen, estimation of, VII, 456, 518
- VAN DEN DRIESSEN MARKEUW.** Estimation of saccharin in cocoa powder, III, 436
- DRINKWATER.** See *Fowles*.
- DRUITT.** Liquid essence of beef, VIII, 392
- DUBIN.** See *Raisiss*.
- DUBOIS.** Carbon disulphide, use of, in the extraction of wines, III, 477  
Salicylic acid, separation of, from tinned tomatoes, III, 486  
Starch, estimation of, in cocoa, VI, 712  
Yellow silk, colouring matter of, VIII, 633  
and **VIGNON.** Poisonous properties of *m*-phenylenediamine, VI, 106
- DUCHÁČEK.** See *Bertrand*.
- DUCLAUX.** Acetic acid homologues, rate of distillation of, I, 519  
Cocoa ash, VI, 698  
Fatty acids in butter fat, II, 280
- DU CLAUXI.** Culture yeast, I, 215
- DUDLEY, W. L.** Spigeline, VI, 235
- DÜGGLI.** Bacteriology of masun, VIII, 227
- DÜRING.** Antimonin, VII, 447
- DULIÈRE.** Constants for croton oil, II, 173
- DUMAS.** Chemical composition of yeast, I, 208
- DUNBAR.** Estimation of tartaric and malic acids, IX, 108  
See *Denis*.
- DUNBAR, P. B. and R. F. BACON.** Estimation of malic acid in fruit, IX, 98
- DUNCAN, W.** Solubility of turpentine oil in acetic acid, IV, 409
- DUNLAP.** See *Mallinckrodt*.
- and **GILBERT.** Fat-splitting enzymes, VIII, 292
- SHENK.** Drying oils, II, 360



- DUNLOP.** Beef and mutton fats, crystallisation of, II, 321, 322  
Halphen's test for cottonseed oil applied to lard, II, 321  
Horse fat and oil, II, 72, 206  
Marrow fat from ox bones, II, 205  
Spermaceti, detection of paraffin in, II, 277  
Sperm oil, constants for, II, 236, 237, 275  
detection of mineral oils in, II, 238, 239  
iodine value for, II, 240  
saponification of, II, 233, 234  
Tallow. Iodine value for, oil, II, 202, 203  
See *Thomson*.
- DUNSTAN.** Composition of linseed cake, II, 326  
See *Cash*.
- and **ANDREWS.** Bilkhaconitine, VI, 271, 273  
Indaconitine, VI, 268
- BLOCH.** Salicylic acid, acid impurities in III, 471  
melting point of, III, 467
- BOOLE.** Vesicating constituent of croton oil, II, 172
- BROWN.** Alkaloid in *hyoscyamus muticus*, VI, 318
- CARR.** Aconitine, commercial, VI, 287  
composition of, VI, 259  
hydrolysis of, VI, 263  
permanganate of, VI, 197  
potassium permanganate test for, VI, 261  
Benzaconine, acetyl derivatives of, VI, 264  
Diacetyl aconitine, VI, 262  
Dibenzoylaconine and tetracetylaconine, VI, 264  
Hydrastine, test for, VI, 567  
Piperovatine in *piper ovatum*, VII, 54  
Pseudaconitine, VI, 270, 271  
Pyraconitine, VI, 265
- CHASTON.** Phytosterol from roots of *scopolia carniola*, II, 485
- HARRISON.** Alkaloidal aurichlorides, VI, 196  
Aurichlorbenzaconine, VI, 264
- HENRY.** Composition of aconitine, VI, 259  
and **AULD.** Identification of  $\alpha$ -dextrose in phaseolunatin, I, 392
- INCE.** Composition of aconitine, VI, 258
- JOWETT.** Aconitine aurichlorides, VI, 261  
periodide, VI, 260  
Methyl aconitine, VI, 263
- RANSOM.** Assay of belladonna root, VI, 314
- READ.** Japaconitine and aconitine, VI, 266
- SHEPHEARD.** Aurochlorcaffeine, VI, 170, 196
- SHORT.** Exhausters, I, 78; II, 4  
Loganin, VI, 468  
Nux vomica, assay of the official preparations of, VI, 473
- TICKLE.** Estimation of aconitine, VI, 282  
and **JACKSON.** Methyl-benzaconine, VI, 265
- DUNSTAN, W. R.** Borax test for glycerol, II, 455
- DUNWODY, R. G.** Turpentine oil, adulteration of, IV, 409  
specific gravity of, IV, 408
- DUPONT.** Refractometer values for lard and its substitutes, II, 319  
and **GUESLAU.** Rose oil, IV, 386
- LABAUNE.** Estimation of geraniol, IX, 329
- DUPOUY.** Detection of heated milk, VIII, 168
- DUPRE.** Nitroglycerin explosives, estimation of water in, III, 593  
Spirits, determination of the fusel oil in, I, 518  
Wines, detection of foreign colouring matters in, I, 180  
See *Girard*.
- DUQUESNEL.** Commercial aconitine, VI, 287
- DURAND.** Detection of saccharin, IX, 289
- HUGUENIN.** Indalizarine and phenocyanine, V, 352  
Muscarin, V, 342
- VON DURAND.** Hydrastine, VI, 564
- DURAND-CLAYE.** Distinction between natural asphalt and coal-tar pitch, III, 64, 65
- DURIEN, E.** Estimation of tannin, V, 92
- DURRANS.** Aniseed oil, IX, 351
- DUTOIT, P. and M. DUBOIX.** Estimation of tartaric, malic and succinic acids, IX, 109
- DUVILLIER, E.** Synthetic betaines, VII, 273  
and **BUTSINE.** Amines in vinasses, VI, 15  
Modification of Hofmann's method for the separation of amines, VI, 7
- DUYK.** Lard oil, specific gravity of the mixed fatty acids from, II, 199  
Methyl alcohol, estimation of, in formaldehyde, I, 93  
Soap, estimation of, in cresylic acid sheep dips, III, 331
- DUYK, M.** Composition of lavender oil, IV, 347
- DVORKOVITCH, P.** Tea, analysis of, VI, 600  
estimation of caffeine in, VI, 608  
of tannin and fermentation-products in, VI, 616
- DYER, BERNARD.** Analyses of chicory, VI, 674
- DYMOND, T. S.** Hyoscyamine in lettuce, VI, 311  
See *Cripps*.
- DYNAMITFABRIK SCHLEBUSCH.** Estimation of glycerol by Shukoff and Schestakoff's method, II, 463
- DYSON.** Estimation of thiocyanates in gas liquor, VII, 554

## E

- EASTES and TERRY.** Analyses of cocoa, VI, 687, 689
- EATON.** Assay of opium, VI, 428
- EBER.** Eseridine, VII, 29  
Meat, tests for decomposition in, VIII, 312, 313  
Rubreserine and eseroline, VII, 26
- EBLER.** Estimation of hydrazine, VI, 26
- ECALLE.** Assay of aconite, VI, 279, 281
- ECKART.** Rhodinol, IV, 261
- ECKERT.** See *Meyer*.
- ECKLES.** See *Shaw*.
- EDELMANN.** See *Brantigam*.
- EDER.** Alkaloids, detection and estimation of, IX, 479
- EDER, J. M.** Tea, analyses of, VI, 599  
estimation of tannin in, VI, 619
- EDLEFSEN.** Morphine poisoning, VI, 437  
Resorcinol, action of, on  $\beta$ -naphthaquinone, III, 338



- EDMED. Investigation of the elaidin reaction for oils, II, 40
- EDSON. Sugar analysis, IX, 49
- EDUARDOFF. Transformation of india-rubber latex into india-rubber, IV, 105
- EDWARDS. See *Orton*  
and ORTON. Estimation of acetic anhydride in acetic acid, IX, 90
- EFFRONT. Non-identity of trehalase and diastase, I, 212  
Oxidising ferment in yeast, I, 212
- EGER. See *Deussen*.
- EHLERT. See *Alden*.
- EHRENBERG. Dimethylamine in poisonous sausages, VII, 352  
Eseramine, VII, 30  
Eseroline, VII, 26
- EHRlich, F. and WENDEL. Separation of valine, leucine and *iso*-leucine, VIII, 25
- EHRSTRÖM. Lotahistone, VIII, 92
- EIBER and HUE. Polymerisation of turpentine, IX, 381
- EIBNER and MUGGENTHALER. Hexabromide test for linseed oil, IX, 191
- EICHENGRÜN. See *Graebe*.
- EICHORN. Beeswax, determination of the saponification value for, II, 253  
Carnauba wax, acid value for, II, 271
- EICHWALD. Analysis of mucin, VIII, 628
- EIGEL, G. Tests for cocaine in the presence of the eucaines, VI, 334
- EIJKMAN. Specific rotation of hydrastine, VI, 567
- EILOART. Reduction of carbon dioxide by potassium cyanide, VII, 474
- EINBECK. Meat extracts, IX, 615
- EINBERG, P. Behaviour of myoctonine with alkali hydroxide, VI, 276
- EINHORN. Benzidine test for blood, VIII, 524  
Ecgonine, oxidation of, VI, 337  
and MARQUARDT. *d*-Cocaine, VI, 338  
PFEIFFER. Disalicylide, III, 499
- EISENSCHMIL and COPTHORNE. Test for fish oils in vegetable oils, IX, 189
- EITNER. Austrian galls, composition of, V, 35  
Pseudo-tannins, IX, 409  
Tannin extracts, adulteration of, V, 104  
determination of colour in, V, 95
- VAN EKENSTEIN, W. ALBERDA and BLANKSMA, J. J. Estimation of aldehydes in essential oils, IX, 336  
See *Lobry de Bruyn*.
- EKIN, C. Commercial quinoline, VI, 154
- EKROOS. Estimation of alkaloids, VI, 180
- ELBORNE, W. Cinchona barks, VI, 480
- ELION. Estimation of sugars, XI, 22
- VON ELK. See *Bonenkamp*.
- ELLENBERGER. Composition of casein, VIII, 121
- ELLINGER. Cadaverine, VII, 348  
Ptomaines, formation of, VII, 343  
Putrescine, VII, 347
- ELLIOTT. Closed oil-tester, III, 125  
Nitroglycerin, solubility of, III, 570
- ELLIOTT, A. H. Estimation of anthracene in tar, III, 286
- ELLIS. Fixed oils, determination of the temperature on the addition of sulphuric acid to, II, 59  
Hardened oils, IX, 123  
nickel in, IX, 125  
Oils, hydrogenation of, IX, 122
- ELLIS, C. J. Estimation of oxalates in cyanide solutions, VII, 493
- ELLRODT. See *Perow*.
- ELSDON. Fatty acids in fats, IX, 118  
See *Liversage*.  
and HAWLEY. Detection of adulteration of linseed oil, IX, 194
- ELVOVE. Volumetric estimation of hydrastine, VI, 569
- ELVOVE, E. Estimation of formaldehyde, I, 569
- ELZE. Farnesol from citronella oil, IX, 346  
in palmarosa oil, IX, 347  
German spearmint oil, IX, 372  
Lavender oils, constituents of, IX, 363
- EMDEN and SCHMITZ.  $\beta$ -Hydroxybutyric acid, estimation of, IX, 578
- EMDE, H. Arecolidine, IX, 480  
Recognition of methylaniline and dimethylaniline, in the presence of each other, VI, 93
- EMERSON. *p*-Hydroxyphenylethylamine, formation of, in the autolysis of pancreas, VII, 346  
Stearic acid, estimation of, in mixtures of fatty acids, II, 394
- EMERY. Opium, assay of, VI, 428  
Specific gravity, calculation of, from Baumé hydrometers, I, 10, 15  
Tin in canned foods, VIII, 339  
See *Schweinitz*.
- EMERY, W. O. Acetanilide and phenacetin, estimation of, in admixture, IX, 472  
and PALKIN, S. Antipyrine, estimation of, IX, 470
- EMICH, F. Glycocholic acid, VII, 412
- EMINGER. Solubility of theobromine, VI, 592
- EMMERLING. Milk-globulin, VIII, 131  
"Yeast-glucose," I, 211
- EMMERT and REINGRUBER. Dimethylnaphthalenes, III, 251
- EMMET and GRINDLEY. Estimation of creatinine, VIII, 397
- ENDEMANN. Asphalt, iodine absorption for, III, 92  
Shellac analysis, IX, 312  
valuation of, IV, 72  
See *Prochaska*.  
and PAISLEY. Driers, II, 360
- ENGEL. Casein, precipitation of, in human milk, VIII, 133  
Elastin, properties of, VIII, 632  
and KIENER. Poisonous effect of toluylene-diamines, VI, 108
- ENGEL, A. See *Tschirck*.
- ENGEL, G. Estimation of indigotin, V, 402
- ENGEL, R. Indicators, III, 552  
Poirrier's soluble blue as an indicator, III, 552
- ENGELAND and KUTSCHER. Formation of agmatine guanidylbutylamine from ergot, VII, 351

- ENGELHARD and LATSCHINOW. Phenol-sulphonic acids, III, 393
- ENGELHARDT. Morphine, estimation of, IX, 508  
and JONES. Cinchona alkaloids, titration of, VI, 498  
Cresotic acid, detection of, in salicylic acid, III, 473  
Morphine sulphate, IX, 497  
WINTERS. Morphine salts, IX, 497
- ENGLER. Petroleum, crude, assay of, III, 48  
formation of, III, 37  
Hanoverian, III, 44  
Viscosimeter, VIII, 606  
and DIECKHOFF. Solubility of cresol in sodium acetate and sodium valerate, III, 331  
UBBELOHDE. Separation of hydrocarbons IX, 232
- ENNIS. Preparation of linseed oil, IX, 180
- ENZ. Aluminium acetate in acetic acid, IX, 91
- EPHRAIM. Hübl process for the determination of the iodine value of fats and oils, II, 31
- EPPINGER, P. Hematoporphyrin, VIII, 552
- EPSTEIN, E. and POLONYI, H. Estimation of paraffins by picrate method, IX, 239
- ERBAN. See *Schmidt*.
- ERDMANN. Alkaloids, test for, VI, 200  
Clove oil, IV, 331  
Coffee, volatile oil of, VI, 650  
Linolenic acid, chemical composition of, IX, 185  
Potassium cyanate, preparation of, VII, 537  
and BEDFORD. Linseed oil, composition of, II, 330  
Linolenic acid of linseed oil, IX, 184  
and HUTH. Alcohol in rose oil, IV, 384
- ERDMANN, E. Methyl anthranilate in essential oils, IV, 364  
and H. Geraniol, detection of, IV, 261  
Methyl anthranilate in neroli oil, IV, 367
- ERDMANN, H. Patent blue V, V, 243  
Sulphur dyes, V, 375
- ERLENBACH. Hair-dye, VIII, 680
- ERLENMEYER. Preparation of potassium cyanide, VII, 473
- ERLICH. See *Benedict*.
- ERMEN. Viscosities of starch solutions, I, 427
- ESCH. Estimation of india-rubber, IX, 321
- ESCHWEILER and NAEPPEN. Preparation of pure trimethylamine, VI, 16
- ESTCOURT, C. Meat extracts, VIII, 396
- ETARD and BEMONT. Decomposition of sodium nitroprusside, VII, 531
- ETIENNE and DELHAYE. Manufacture of meat extracts, VIII, 392, 396
- ETTI. Test for vanillin, III, 516
- ETTI, C. Tannin of oak-bark, V, 24, 25, 26
- EUGLING. Presence of casein in milk in combination with tri-calcium phosphate, VIII, 119
- EULER. Presence of acid in the determination of the activity of invertase, VIII, 8
- EVAN. Aconite, assay of, IX, 489  
Copaiba, adulteration of, IX, 313  
Cyanates, estimation of, VII, 541
- EVANS, A. C. See *E. G. Hastings*.
- EVANS, JOHN. Guaiacum, IV, 65; IX, 311
- EVERS. Bellici's test for Arachis oil, IX, 126  
Crude storax, analysis of, III, 463  
Linseed oils, differentiation between boiled and unboiled, II, 357  
Turpentine oil, examination of, IV, 422  
See *Liversege*.
- EWAN. Estimation of sulphides in commercial cyanide, VII, 488
- E'WE and VANDERKLEED. Morphine, estimation of, IX, 508
- EWELL, Cocoa powder, analysis of, VI, 691  
Sugar in coffee, VI, 643  
See *Wiley*.  
and PRESCOTT. Phenol, detection of cresylic acid in, III, 317  
Salicylic acid, acid impurities in, III, 471  
estimation of cresotic acid in, III, 473, 474
- EWERS. Polarimetric estimation of starch, I, 425
- EWINS. Cytisine, constitution of, IX, 534  
and LAIDLAW. Indolethylamine, VII, 351  
PYMAN. Formation of  $\beta$ -iminazolyethylamine from histidine, VII, 350
- EWINS, A. J. See *George Barger*.
- EYKMAN. Macleyine, VI, 353  
Scopoletin, VII, 34  
Spirit of nitrous ether, composition of, I, 243
- EYNON. See *Ling*.
- EYRE. Cultivation of flax and hemp, IX, 180  
See *Armstrong*.

## P

- PABINYI. Morphine, colour test for, IX, 497
- PABRIS. Estimation of glycerol in wines, I, 167  
See *De Negri, Villareschia*.
- PABRIS, G. Bergamot oil, IV, 318
- PAHLBERG and LIST. Preparation of saccharin, III, 428  
REMSEN. Preparation of saccharin, III, 428
- FAHRION. Dégras, composition of, II, 505  
Linseed oil and blown oils, IX, 202  
composition of, II, 330; IX, 185  
drying of, II, 347, 349; IX, 199  
specific gravity of, IX, 187  
Oils, drying of, II, 36
- FAHRION, W. Abietic acid, IV, 22, 23  
American rosin, composition of, IV, 22
- FAHRNSTEINER. Use of benzene in Muter's estimation of fatty acids, II, 392
- FAIST. Composition of sheep's wool, VIII, 683
- FAJANS. Colourimetric estimation of salicylic acid, III, 484
- FALK. See *Sherman*.
- FALK, GEORGE. Animal bases, IX, 560
- FALKSON, G. Cocamine, VI, 340
- FANTO. Glycerol, estimation of, in oils and fats II, 477  
in soap-lyes, II, 478  
Triglycerides, saponification of, II, 13  
See *Zeisel*.
- FARGAS, M. Effect of caffeol on the heart's action, VI, 650
- FARNER. See *Tschirch*.

- FARNSTEINER.** Almond oil, composition of, II, 102  
 Beef and mutton tallow, unsaturated acids in, II, 208  
 Cacao butter, percentage of saturated acids in, II, 177  
 Elaidin reaction for oils, II, 40  
 Lard, composition of, II, 317  
 Sesame oil, detection of cottonseed oil in, II, 146
- FARNSTEINER, K.** Soluble ash of cocoa, VI, 706, 707
- FARR.** See *Braithwaite*.  
 and **WRIGHT.** Cinchona alkaloids, titration of, VI, 498  
 Colchicum seeds, assay of, VII, 9  
 Coniine in hemlock, assay of, VI, 223  
 Jaborandi, preparation of tincture of, VII, 51  
 Lobelia, assay of, tincture of, VI, 225  
 Opium, assay of, VI, 424  
 Stramonium seeds, alkaloids in, VI, 319
- FARRELL and GOLDSMITH.** Estimation of prussian blue in silk, VIII, 660
- FASAL.** Estimation of tryptophan, VIII, 87
- FASSBENDER and KERN.** Extraction of linseed oil from linseed, II, 326
- FAULDING.** Estimation of cineol in eucalyptus oils, IV, 339
- FAUST.** Isolation of sepsine from putrid yeast, VII, 353
- FAWCETT, J.** Use of piperazine to dissolve uric acid calculi, VII, 200
- FAWSITT.** Driers, II, 360  
 Estimation of basic substances in wood naphtha, I, 102  
 See *Dittmar*.
- FAWSSETT, T.** Bromo-derivatives of cinchona alkaloids, VI, 506
- FEDER.** Water-content of sausage, IX, 619
- FEDER, E.** Estimation of picric acid, V, 123
- FREMSTER, J. H.** Caffeine in guarana, VI, 683
- FEIGERLE.** See *Valenta*.
- FEILMANN, E.** See *W. P. Dreaper*.
- FEINBERG.** Apomorphine, IX, 499  
 Estimation of aldehydes, IX, 287
- FEIST.** Calumba, VI, 575  
 Strophanthidine, formula of, VII, 122  
 Tannin, constitution of, V, 17, 19
- FELD.** Cyanogen, estimation of, in spent gas purifying mass, VII, 521  
 Thiocyanates, estimation of, VII, 555
- FELDBAUS.** Estimation of cyanogen contents of bitter-almond and cherry-laurel water, VII, 466  
 Occurrence of vegetable alkaloids, VI, 168
- VON FELLEBERG.** Estimation of salicylic acid, IX, 302
- FELS, J.** Glue, determination of the strength of, VIII, 613  
 test for, VIII, 607  
 viscosity of, VIII, 606
- FENAROLI.** Ozone absorption of linseed oil, II, 339  
 values for fixed oils, II, 38
- FENDLER.** Candle nut oil, II, 149  
 Floricin, composition of, II, 165  
 India-rubber, estimation of, IX, 321  
 Linseed oil, unsaponifiable matter in, II, 333  
 Sperm oil, fatty acids from, II, 235  
 saponification of, II, 233  
 See *Thoms*.
- FENDLER, G. and FRANK, L.** Estimation of fatty acids in soap, IX, 206
- FENTON.** Test for carbohydrates, I, 302  
 and **SISSON.** Detection of formic acid by reduction to formaldehyde, I, 521
- FENTON, H. J. H.** Detection of tartaric acid, I, 538  
 and **BARR, G.** Colour reactions for organic acids, I, 486
- VON FERENTZY, J.** Estimation of tartaric acid in fruit juices, IX, 107
- PERIC.** See *Partheil*.
- FERNBACH, A.** Isolation of tannase, III, 526
- FERRIER, C.** Estimation of sulphur compounds in soap-lye glycerin, II, 469
- FESCA and IMAI.** Ash of Japanese tobacco, VI, 243  
 Mode of existence of the nitrogen in tobacco, VI, 244
- FEUERSTEIN and LIEBERMANN.** Isomer of gallein, V, 299
- PICKENDEY.** Analysis of india-rubber latex, IX, 320
- FIEHE.** Detection of invert sugar in commercial honey, I, 386
- FIELD, W.** Estimation of sulphur in wood pulp, IX, 84  
 See *Barger, Blum*.
- FIGUIER.** Formation of ammonium cyanide, VII, 472
- FILSINGER.** Cocoa butter, iodine absorption of, VI, 702  
 Linseed oil, rotation of, II, 338, 339  
 Silk, action of alkaline copper hydroxide in glycerin on, VIII, 639  
 Tussah silk, microscopical character of, VIII, 641
- PINCK.** See *Wallenstein*.
- PINCKE.** Fibre in cocoa husks and powder, VI, 696  
 Formic acid in acetic acid, IX, 91  
 Pyridine, estimation of, IX, 476
- FINE, M. F.** Uric acid, estimation of, IX, 571, 572
- PINKENBEINER.** See *Blank*.
- PINKENER.** Castor oil, detection of adulteration of, II, 162  
 Fats and oils, determination of the solidification points of, II, 57  
 Linseed oils, differentiation between boiled and unboiled, II, 357  
 Rosin oil, detection of, in lubricating oil, III, 174
- PINZELBERG.** Use of piperazine to dissolve uric acid calculi, VII, 200
- PIORE.** See *Rogier*.
- PIRBAS.** Solanidine, VII, 92  
 Solanine, formula for, VII, 90  
 preparation of, from potato, VII, 89

- FISCHER. Melting point of dextrose phenyl-osazone, I, 373  
of salicylic acid, III, 467  
and ABDERHALDEN. Amino-acids formed by the hydrolysis of caseinogen, VIII, 20  
Digestion of proteins, VIII, 471  
Polypeptides obtained by the hydrolysis of proteins, VIII, 471  
BÖDEKER. Composition of chondrin, VIII, 625  
DÖRPINGHANS. Amino-acids formed by the hydrolysis of keratin from ox-horn, VIII, 20  
GRUENERT. Detection of benzoic acid in meat and fats, IX, 281  
HARRIES. Boiling point of glycerol, II, 447  
Fractional distillation of essential oils, IV, 224  
HELPERICH. Glucosides, synthetic, IX, 545  
HEPP. Induline, 3B, 6B, v, 327  
Indulines, production of, v, 326  
KOERNER. Fluorescence of harmine, VII, 36  
LEVENE and ADERS. Amino-acids formed by the hydrolysis of gelatin, VIII, 20  
PASSMORE. Extraction of phenylhydrazine from sugar phenylhydrazides, VI, 33  
PAYNE. Halphen's colour test for cottonseed oil, II, 135  
PILOTY. Formation of gulonic acid from saccharic acid, VII, 397  
SCHELLENS. Determination of the water in lard, II, 320  
TÄUBER. Formation of *p*-aminophenyl- $\gamma$ -lepidine, v, 359  
FISCHER, B. Detection of cresotic acid in salicylic acid, III, 472  
Use of dimethyl-amino-azobenzene as an indicator, v, 135  
FISCHER, C. S. Estimation of glycocoll, VII, 211  
FISCHER, E. Amines, tertiary, recovery of from their acid ferrocyanides, VI, 10  
Amino-acids, isolation of, VII, 218  
Caseinogen, amino-acids formed by the hydrolysis of, VIII, 20  
Meat, nitrogenous extractives of, VIII, 286  
Phenylhydrazine hydrochloride, use of, for the detection of aldehydes, I, 255  
Protein digestion products, preparation of, VIII, 470  
Proteins, VIII, 17  
Purine and its derivatives, synthesis of, VI, 579  
Skatole, detection of, VII, 254  
Tannins, constitution of, IX, 385  
Trehalase and diastase, identity of, I, 212  
Uric acid, formulæ of, VII, 364  
Xanthine, preparation of, VII, 328  
FISCHER, E. and O. Rosolic acid and aurin, v, 260  
SKITA. Decomposition products of fibroin and serine, VIII, 637  
Silk fibroin, VIII, 92  
FISCHER, K. and GRUENERT, O. Extraction of benzoic acid from flesh products, III, 411  
FISCHER, O. and BEDALL. Formation of *p*-aminophenyl- $\gamma$ -lepidine, v, 359  
BESTHORN. Formation of *p*-aminophenyl- $\gamma$ -lepidine, v, 359  
RUDOFF. Formation of *p*-aminophenyl- $\gamma$ -lepidine, v, 359  
FITZPATRICK, R. M. Estimation of moisture in soaps, IX, 204  
FLAMAND. Detection of saccharin, IX, 289  
FLANDERS. See *Folin*.  
FLATAU and LABBÉ. Citral and citronellal, separation of, IV, 273  
Geraniol and citronellol, separation of, IV, 259, 264  
Oleic acid in geranium oils, IV, 344  
Sweet-orange oil, composition of, IV, 359  
VON FLEISCHL. Hammometer, VIII, 563  
FLEISCHMANN and MORGEN. Calculations for the analysis of milk, VIII, 163  
FLEISSIG. Tolu balsam, IX, 297  
FLEROFF. Parahistone, VIII, 92  
FLETCHER. See *Allen*.  
and HOPKINS, GOWLAND. Test for lactic acid, VII, 435  
FLETCHER, F. W. Citrate of iron and quinine, VI, 532  
FLEURENT. Gliadin ratio of flours, I, 455  
FLEURY. Detection of benzoic acid, IX, 280  
Test for wine vinegars, IX, 94  
FLEURY, G. Test for morphine, VI, 382  
FLORENTIN. See *King*.  
FLORIO. Solubility of morphine, VI, 375  
FLÜCKIGER. Atropine, test for, VI, 306, 307  
Bdellium, IV, 100  
Elemic acid, IV, 5  
Gerrard's test for atropine, VI, 306  
Ipecacuanha, assay of, VII, 44  
Lyaconine, VI, 274  
Mastic, essential oil from, IV, 59  
Opium, analysis of, VI, 409, 419  
Pomegranate alkaloids, VI, 230  
Strychnos alkaloids, VI, 441  
Trapeines, test for, with phenolphthalein, VI, 305  
FLÜRSCHHEIM. Quinocarbonium salts, v, 238  
FLURY. Physiological properties of harmaline, VII, 36  
V. PODOR. Acids in butter fat, IX, 152  
FOERSTER, F. Estimation of camphor, IV, 199  
FOERSTER, P. Detection of colophony, IV, 29  
FÖRSTER. See *Mylius*.  
FOERSTERLING, HANS. Preparation of cyanogen bromide, VII, 461  
and PHILIPP. Formation of urea from cyanamide salts, VII, 557  
FOKIN. Driers, II, 360  
Linseed oil, composition of, II, 330  
Oils, drying of, II, 348  
Oleic acid, reduction of, with colloidal platinum, II, 375  
FOKIN, S. Determination of hydrogen number of unsaturated compounds, IX, 237  
FOKKER, A. P. Detection of carbon monoxide in blood, VIII, 534  
FOL. Examination of dyed fibres, v, 486

- FOLIN.** Creatine, estimation of, IX, 566  
Creatinine, estimation of, VII, 315; VIII, 397, 410; IX, 566, 611  
Cystine, isolation of, in the hydrolysis of proteins, VIII, 22  
Meat extract and yeast extract, detection of, VIII, 418  
foods, estimation of ammonia in, IX, 612  
Urea, estimation of, VII, 299  
Urine, estimation of acetone in, I, 109  
of ammonia in, IX, 564  
of creatinine in, VIII, 410  
and **DENIS.** Tyrosine, estimation of, IX, 563  
Uric acid, estimation of, IX, 571, 572, 573, 574  
Vanillin, estimation of, IX, 307  
Benzoic acid, estimation of, IX, 283  
Hippuric acid, estimation of, IX, 569  
**SCHAFER.** Estimation of uric acid, VII, 370  
**FORBES and KEITH.** Phosphorus compounds in animal metabolism, IX, 611  
**DE FORCRAND.** Phenates and phenoxides, III, 294  
**FORD.** Effect of acid or alkaline impurities on hydrolysis by enzymes, VIII, 8  
**FORDOS and GELIS.** Estimation of cyanogen in cyanides, VII, 483  
**FOREMAN, P. W.** Estimation of aspartic and glutamic acids in protein hydrolysis, IX, 592  
Proteins of linseed, VIII, 110  
**FORMAN.** See *LaWall*.  
**FORMANEK.** Absorption spectra of colouring matters, v, 438, 648  
Eosins, absorption spectra of, v, 297  
Methæmoglobin, spectrum of, VIII, 541  
**FORMENTI.** Detection of saccharin in milk, III, 433  
**FORREST, C. N.** Tests for bituminous road materials, III, 101  
See *Gill*.  
**FORSTER.**  $\beta$ -derivatives of camphor, IV, 202  
Protein matter of cocoa, VI, 698  
and **RIEHELMANN.** Alkaloid in coffee, VI, 647  
**FORTEY.** See *Sydney Young*.  
**FORTH, H.** See *J. R. Ashwell*.  
**FORTINI.** Saponification, IX, 118  
**FORTMANN, G.** See *F. Russig*.  
**FOSTER and LAMBERT.** Gastric juices, IX, 581  
**FOUCHET, A.** Walnut oil, IX, 145  
**FOUQUET, A.** Cigar smoke, VI, 252  
**FOURNEAU.** See *Willstätter*.  
**FOWLER, H.** Manufacture and properties of commercial acetylene, III, 89  
**FOWNES and DRINKWATER.** Specific gravity of aqueous ethyl alcohol, I, 110  
**FOX,** Blown oils, II, 362  
Linseed oil, drying of, II, 344  
See *Dobbie*.  
and **BAYNES.** Blown oils, II, 362  
**FOX, J. J. and SAGEMAN, P. J.** Caffeine, tea and coffee, VI, 579; IX, 525  
**FOX, W.** Value of a non-mineral lubricating oil, III, 163  
**FRABOT.** See *Jean*.  
**FRADISS.** Test for caramel, v, 640  
**FRANCESCONI and BARGELLINI.** Detection of fluorescence I, 40  
**FRANCIS.** Determination of the diastatic power of enzymes, VIII, 5  
Formation of hydrocyanic acid in tropical plants, VII, 462  
See *Trowbridge*.  
and **YOUNG.** Action of nitric acid on iso-paraffins, IX, 238  
Paraffins, III, 3  
Polymethylenes, IX, 236  
**FRANÇOIS.** Assay of kola, IX, 532  
Separation of methylamine and ammonia, VI, 18  
**FRANÇOIS, M.** Estimation of pyridine, VI, 137  
**FRANK.** Decomposition of calcium cyanamide by superheated steam, VII, 557  
See *Green*.  
and **CARO.** Formation of barium cyanide by passing nitrogen over barium carbide, VII, 557  
**JACOBSON.** Estimation of sulphides of antimony and mercury in rubber, IV, 142  
**MARCKWALD.** Acetone extraction of rubber, IV, 124  
Analysis of vulcanised rubber, IV, 132  
**PERKIN.** Estimation of indigo, in presence of starch, IX, 446  
**FRANK, F.** Determination of the gas value of an oil, III, 140  
**FRANK, L.** See *G. Fendler*.  
**FRANKEL and KELLY.** Hydrolysis of chitin, VIII, 671  
**FRANKFORDER.** See *Frend*.  
and **HARDING.** Unsaponifiable matter in wheat oil, II, 147  
**FRANKFORDER, G. B. and WEST, R.** Gasometric method for the estimation of formaldehyde, I, 262  
**FRANKFURT.** See *Schulze*.  
**FRANKLAND and MACGREGOR.** Production of sarcolactic acid, VII, 449  
**FRANZ.** See *Rost*.  
and **ADLER.** Test for arachis oil, IX, 129  
**FRANZ, A.** Detection of chicory in coffee, VI, 671  
**FRASER and GARDNER.** Estimation of cholesterol, IX, 224  
**FREHSE.** Detection of saponin in beverages, VII, 129  
**FRERICH and HARNACK.** Apomorphine hydrochloride, VI, 388  
**FRERICH.** See *Beckurts, Behre*.  
**FRERICH, G.** Pyroligneous acid, IX, 96  
and **TAPIS, N. DE FUENTES.** Emetine percentage composition of, VII, 39  
Ipecacuanha, assay of, VII, 45  
percentage of alkaloids in, VII, 48  
**FRESENIUS.** Assay of pyrolignite and lead acetate, I, 512  
Detection of colouring matters in food, v, 652  
and **MAKIN.** Estimation of phenols in soap, III, 334  
**FRESENIUS, C. and POPP.** Estimation of boric acid in meat extracts, VIII, 425

- FRESENIUS, W. and GRÜNHUT, L.** Acetate of lime, assay of, I, 510  
Citric acid, estimation of, IX, 114  
Formaldehyde, estimation of, I, 261  
Prussian blue, solubility of, in ether and chloroform, VII, 507  
Salicylic acid, estimation of, III, 480, 482
- FREUDENBERG.** Formation of calcium cyanamide by passing nitrogen over calcium carbide, VII, 557
- FREUND.** Berberine, conversion of, to hydrastinine, IX, 521  
Cevine oxide, VII, 76  
Cytisine, constitution of, IX, 534  
Hydrastine, VI, 564  
Meconin in *hydrastis canadensis*, VI, 410  
Morphothebaine, VI, 406  
Thebaine, constitution of, VI, 356  
and **BECK.** Aconitine, composition of, VI, 258  
hydrolysis of, VI, 263  
Japaconitine and aconitine, identity of, VI, 266  
**BECKER.** Constitution of cotarnine, VI, 358  
**FRANKFORTER.** Constitution of narceine, VI, 360  
**JOACHIM.** Globulin, VIII, 91  
**NIEDERHOFHEIM.** Pseudoaconitine, VI, 271  
**WILL.** Specific rotation of hydrastine, VI, 566
- FREUDENBERG.** Formation of calcium cyanamide, VII, 557
- FREUNDLER, P.** Detection of methyl anthranilate in essential oils, IV, 364
- PREY.** Columbic acid, VI, 577  
See *Smith*.
- FREYER.** Estimation of salicylic acid, III, 480
- FRICKE, E.** Substitute for coffee, VI, 664
- FRIEDEL.** Formation of acetophenone, III, 427  
and **CRAFTS.** Formation of acetophenone, III, 427
- FRIEDENTHAL.** Separation of casein from milk, VIII, 184
- FRIEDHEIM.** Precipitation of casein in milk of asses, VIII, 133
- FRIEDLÄNDER.** Quinonoid constitution of phenolphthalein, v, 263
- VON FRIEDRICHS.** Opium, adulteration of, IX, 504  
Myrrh, IX, 318
- FRIEND.** Drying of linseed oil, IX, 199
- FRIESE.** Detection of benzoic acid in fats, IX, 282
- FRISTEDT.** See *Mörner*.
- FRISWELL.** Specific gravity of commercial o-toluidine, VI, 67
- FRISWELL, R. J.** Fractional distillation of aniline oils, VI, 80
- FRITSCH.** Synthesis of meconin, VI, 410
- FRITZ and ZYMANDI.** Values for oxidised linseed oil, IX, 200
- FRITZSCHE.** Determination of the mean molecular weights of soluble and insoluble fatty acids from butter, II, 288  
Saponification value for Danish butter, II, 286
- PROIDEVAUX.** Salicylic acid in preserved eggs, IX, 620
- FROMM.** Composition of artificial bitter-almond, water, III, 426
- FROMME.** Ergot, estimation of alkaloids, VII, 22  
Opium, assay of, VI, 421  
Pilocarpine, estimation of, VII, 53  
Pomegranate alkaloids, estimation of, VI, 231  
Estimation of cinnamein in Peruvian balsam, IX, 296
- FROMMER.** Acetone, detection of, I, 105; IX, 577
- FRÜHLING.** Exhauster for the estimation of oils and fats, II, 5
- FRÜHLING, R.** Fat of horse flesh, VIII, 379
- FRÜLING.** Cane sugar, estimation of, in the presence of raffinose, I, 569
- FRYER.** See *Kohn*.
- FUCHS.** Boiling point of acetone, I, 105  
of ethyl alcohol, I, 110  
of methyl alcohol, I, 86  
See *Abderhalden, Csilyhany*.
- FÜHNER.** Colchicine derivatives, activity of, IX, 534  
Toxicological detection of aconite, IX, 489
- FÜRSTENBERG.** See *Sprinkmeyer*.
- VON FÜRTH.** Blood stains, test for, VIII, 572  
Egg mucin, VIII, 92  
Hæmoglobin, occurrence of, VIII, 506  
See *v. Csilyhany*.
- and **CHARNASS.** Estimation of lactic acid, VII, 439
- JERUSALEM.** Estimation of tyrosinase, VIII, 14
- FULD.** Albumose, VIII, 91  
Change of casein into paracasein, VIII, 127  
See *Blum, Spiro*.
- and **LEVISON.** Estimation of the proteoclastic power of pepsin, VIII, 494
- FULDA.** See *Reverdin*.
- FULLER, H. C.** Cocaine, IX, 494  
See *L. F. Kebler*.
- FUNK.** See *Abderhalden*.
- FUNKE.** Preparation of oxyhæmoglobin, VIII, 507

## G

- GABUTTI.** Detection of abrastol in wines, III, 402
- GADAIS, L. and J.** Analysis of calcium citrate and lemon juice, I, 563; IX, 110
- GADAMER.** Berberine, constitution of, VI, 552  
Calumba, VI, 575  
Mustard oil, estimation of allyl-thiocarbimide in, IV, 301  
Tea, estimation of caffeine in, VI, 609  
l-Tetrahydroberberine, identity of, with canadine, VI, 574
- GADD, H. W. and S. C.** Assay of belladonna and its preparations, VI, 316
- GAEBEL.** Constitution of hordenine, VII, 36
- GAIR, DICKENSON.** Estimation of naphthalene in coal-gas and spent oxide of iron, III, 246
- GALEOTTI.** Precipitation of proteins by salts, VIII, 37
- GALIPPE.** Cocoa ash, VI, 698
- GALLETLY.** See *Spence*.



- GAMGEE.** Carbon monoxide, extraction of, from carboxyhaemoglobin, VIII, 530  
 Haemoglobin, occurrence of, VIII, 506  
 preparation of, VIII, 508, 509  
 spectrum of, VIII, 514  
 Oxyhaemoglobin, specific conductivity of, VIII, 511  
 and **CROFT-HILL.** Rotation of haemoglobin, VIII, 36, 71  
**JONES.**  $\alpha$ -Nucleoprotein, VIII, 92  
 Nucleoproteins, rotation of, VIII, 36  
 Proteins, rotation of, VIII, 77
- GAMS.** See *Pictet*.
- GANE and WEBSTER.** Adulterants of turpentine oil, IV, 428
- GANSSEER, E.** See *Häfner*.
- GANTTER, F.** Hide-clippings, valuation of, for glue-making, VIII, 613  
 Tannin assay, oxidation method of, V, 68
- GARDNER.** Drying oils, IX, 184  
 Fustic as a mordant-dye, V, 410  
 Haematoxylin, V, 403  
 Oils and paints, effect of storage on, IX, 196  
 Linseed oil, effect of pigments ground in, IX, 197  
 See *Buckmaster, Fraser, Green, Marsh.*  
 and **CARTER.** Wool-gelatin, VIII, 684  
**DENTON.** Extraction of indirubin, V, 397  
**HODGSON.** Estimation of tannins, V, 93
- GARDNER, J. ADDYMAN.** Cholesterol, II, 479; IX, 223  
 Phytosterol, II, 479  
 and **BUCKMASTER, GEORGE ALFRED.** Haemoglobin and its derivatives, VIII, 497
- GARDNER, W. M.** Colouring matters of natural origin, V, 383; IX, 427
- GARNETT, H.** Estimation of citral in essential oils, IV, 270
- GARRETT, F. C.** Asphalt, analyses of, III, 88  
 Clay, absorption of non-bituminous matter by, III, 84  
 Hydrocarbons, III, 1
- GARROD.** Detection of haematoporphyrin in urine, VIII, 555  
 See *Orton*.
- GARSED, WILLIAM.** Assay of coca leaves, VI, 347
- GARSEL, W. and COLLIE, J. N.** Estimation of cocaine as di-iodo-cocaine hydriodide, VI, 349
- GASCARD.** See *Georges*.
- GASCH, R.** Assay of ferrocyanide melt, VII, 514
- GASPARINI.** Estimation of sulphur in rubber, IX, 323
- GASSLER.** Analyses of German resin soaps and Sinclair's soap, II, 442
- GASTALDI, E.** Modification of Halphen's test for butter-fat, IX, 154  
 Test for cottonseed oil, IX, 135  
 See *C. Pertusi*.
- GATTERMANN.** Constitution of primuline, V, 371  
 Taste reaction of hydrocyanic acid, VII, 465
- GAUNT.** Estimation of alcohol by the freezing-point method, I, 129
- THOMAS and BLOXAM.** Preparation of indigotin, V, 386
- GAUTIER.** Flesh, poisonous, VIII, 320  
 Hops, destruction of organic matter in, VII, 187  
*p*-Hydroxyphenylethylamine, formation of, in putrid cod-livers, VII, 346  
 Opium smoke, VI, 433  
 Xanthine, synthesis of, VII, 328  
 and **MOURGUES.** Butylamine and hexylamine from cod-liver oil, VII, 352  
 Isolation of hydrolutidine from cod-liver oil, VII, 353
- GAWINSKI.** Estimation of oxyproteic acids in urine, VII, 407
- GAY.** See *Stillzer*.
- GAYER.** Species of aconitum, VI, 253
- GAYLORD, H. R. and AVERILL.** Permanency of coloured inks to light, IX, 466
- GAY-LUSSAC.** Preparation of cyanogen, VII, 454
- GAZE.** Purification of berberine, VI, 553
- GAZE, R.** Estimation of cinchona alkaloids, IX, 514
- GEBHARDT.** Loss of colour of dyed fabrics, when exposed to light, V, 484
- GEER, W. C.** Analysis of turpentine oils by fractional distillation, IV, 419
- GEERLIGS.** Sugar analysis, IX, 49
- GEHE and Co.** Assay of pomegranate bark, VII, 50
- GEIGY, J. R.** Dyestuffs from 2:6 dichlorobenzaldehyde, V, 242
- GEISEL.** Permanganate of cocaine, VI, 197
- GEISLER, J. F.** Opium, assay of, VI, 426  
 Tea, analyses of, VI, 600, 623  
 estimation of tannin in, V, 67
- GEITEL.** Borneo tallow, II, 176  
 Triglycerides, saponification of, with alkali, II, 12  
 and **VAN DER WANT.** Japanic acid and Japan wax, II, 193
- GELIN.** See *Kling*.
- GELIS.** See *Fordos*.
- GEMMELL.** Hexabromide test for linseed oil, IX, 191  
 Insoluble bromide test for fats, IX, 119
- VON GENERSICH, W.** Benzoic acid, estimation of, in foods, III, 412  
 Salicylic acid, detection of, III, 479  
 estimation of, III, 480
- GENTH.** Detection of saccharin, IX, 289
- GENTHE.** The drying of linseed oil, II, 36, 348
- GENVRESSE and LANGLOIS.** Vetivene, IX, 347
- GEORGES.** Estimation of caffeine in tea, VI, 611  
 and **GASCARD.** Estimation of morphine, VI, 386, 433
- VON GEORGIEVICS.** Homolka's base, V, 235
- GEPHART and LUSK.** Meat rations, IX, 619
- GEPPERT.** Antidotes for cyanide poisoning, VII, 470
- GÉRARD.** Phytosterol from brewer's yeast, II, 486  
 Phytosterols of cryptogams and phanerogams, II, 487  
 Uric acid, fermentation of, VII, 364  
 See *Abelous, Darcey*.



- GERBER.** Atropine and hyoscyamine, derivatives of, IX, 490  
 Fat, estimation of, in cream, VIII, 187  
 Rennet coagulation, compounds which retard, VIII, 130
- GERDA.** See *Troili-Petersson*.
- GERET.** Bouillon cubes, IX, 617  
 See *Hahn*.
- GERGERS and BAUMANN.** Compound of guanidine with mercuric oxide, VII, 306
- GERHARD.** Lupine alkaloids, VI, 225
- GERHARDT.** Preparation of benzoic anhydride, III, 417
- GERLACH.** Specific gravity of aqueous solutions of glycerol, II, 448  
 See *Brix*.
- GERLAND.** Indigo, extraction of, IX, 429  
 Indigotin, estimation of, V, 393, 400
- GERMAIN.** Sparteine, constitution of, IX, 483
- GERMAN** imperial decree for the analysis of wines, I, 165
- GERMANN.** See *Tschirch*.
- GEROCK.** Estimation of the alkaloids in nuxvomica, VI, 471  
 See *Schneegans*.
- GERRARD, A. W.** Atropine, preparation of, from belladonna, VI, 295  
 test for free, VI, 305  
 Cytisine, VII, 15  
 Gelsemine, formula for, VII, 32  
 Hyoscyamus, assay of leaves of, VI, 317  
 Menthol, purification of, IV, 283
- GERRESHEIM.** Ammonia, removal of, from a mixture with pyridine, IX, 475
- GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE BASEL.**  
 Pyrogene greens, V, 380  
 yellow M, olive N, V, 376  
 Thiophenol black T extra and pyrogene black, V, 377
- GEWIN.** Rennet-enzyme, VIII, 126, 129
- GIANOLI.** Examination of raw silk, VIII, 640
- GIBBS.** Estimation of free salicylic acid in oil of gaultheria, III, 496  
 of methyl salicylate in foods and drugs, III, 493  
 and **HARE.** Effect of pyrogallol on the heart's action, III, 538
- GIBSON.** See *Pringsheim, Vulte*.
- GIES.** Collagen, VIII, 91  
 See *Cutter, Hawk, Richards*.
- GIESEL.** Benzoyl-pseudotropine, VI, 341  
 See *Liebermann*.
- GIESEL, F.** Test for cocaine by formation of the permanganate, VI, 324
- VAN GIJN and VAN DER WAERDEN.** Adulteration of quebracho, IX, 398
- GILBERT.** Detection of colophony in oil of cassia, III, 446  
 See *Dunlap, Lawes*.
- GILDEMEISTER.** Oil of copaiba, IX, 315  
 and **HOFFMANN.** Bergamont oil, cause of the green colour of, IV, 316  
 Cedar-leaf oil, IV, 327  
 Cubeb oil, rotation of, IV, 333  
 Cumic aldehyde, IV, 334
- GILDEMEISTER and HOFFMAN.** Geranium oils, IV, 344  
 Juniper oil, IV, 346  
 Mace oil, specific gravity of, IV, 358  
 Oil of cassia, III, 445  
 of cinnamon, III, 443  
 of copaiba, optical activity of, IV, 87  
 of pimento leaves, IV, 378  
 Wormseed oil, specific gravity of, IV, 427
- GILES.** Change of colour of potassium thiocyanate when heated, VII, 546
- GILL.** Lubricating oils, determination of the loss by heating of, III, 159  
 Oils, determination of the liability of, to inflame spontaneously, II, 512  
 Phenol 2:4-disulphonic acid, preparation of, III, 397  
 Sugar analysis, IX, 49  
 Sugar-cane, analysis of different portions of, I, 359  
 See *Wright*.
- and **FORREST.** Hydrocarbons from distilled wool-grease, IX, 228
- HATCH.** Bromine thermal process for oils and fats, II, 61
- LAMB.** Constants of linseed oil, II, 350
- MASON.** Constants for distilled grease oleines, II, 503
- ROWE.** Constants for neatsfoot oil, II, 201  
 tallow oil, II, 202
- TUFTS.** Phytosterol, effect of exposure to air on the melting point of, II, 489  
 from maize oil, II, 486  
 in oils used for dyeing processes, II, 511  
 Sitosterol, presence of, in the unsaponifiable matter from maize oil, II, 140
- GILL, AUGUSTUS H.** Cloth oils, IX, 228  
 Wool-fat and dégras, (U. S.), II, 495  
 -grease, II, 495; IX, 228
- GILLETTE.** Analysis of lubricating greases, III, 175
- GILPIN.** See *Day*.
- GINSBERG.** Estimation of oxyproteic acids in urine, VII, 407
- GIORDANI.** Crystalline compound from angelica oil, IV, 310
- GIRARD and CUNIASSE.** Estimation of higher alcohols in potable spirits, I, 192
- DUPRÉ.** Detection of coal-tar colours in food, V, 643  
 Detection of colouring matters from meat products, VIII, 383
- LINET.** Analysis of india-rubber latex, IV, 106
- PABST.** Absorption-spectra of coal-tar dyes, V, 438
- GIRARD, A.** Estimation of tannin and colouring matter in wine, V, 86
- GIRAUD.** Composition of gum tragacanth, I, 444  
 Reduction of indigotin, V, 387
- GJALBÄK.** See *Henriques, Sørensen*.
- GLADDING.** Acetate of lime, assay of, I, 509  
 Resin and fatty acids, separation of, IV, 33  
 Rosin, estimation of, in printing ink, IX, 459  
 See *Stillwell*.

- GLADHILL. Analysis of pepper, VII, 64
- GLADSTONE, W. H. Cærulein, IV, 252  
and HIBBERT. Melting point of india-rubber, IV, 108
- GLÄSSNER. Rennet enzyme, VIII, 126
- GLASER. Indicators, III, 552
- GLASMANN. See *Roesler*.
- GLASSMANN. Estimation of dextrose with mercuric solution, I, 338
- GLÉNARD. Emetine, VII, 38
- GLIMMAN, G. Composition of dammar resin, IV, 60  
See *Tschirch*.
- GLOVER, W. H. Constitution of fenchone, IV, 211  
 $\alpha$ -Methyl camphor,  $\beta$ -sulphonamide and anhydramide of, IV, 210  
Naphthylamines, pyridine, guinoline and acridine bases, VI, 111
- GLUECKSMANN. Constitution of tannic acid, V, 19
- GLYNSKY. Apparatus for fractional distillation, I, 21
- GNEHM. Adulteration of raw silk with fat, VIII, 640  
and BLUME. Silk-weighting, VIII, 660  
KAUFLER. Estimation of methyl alcohol in formaldehyde, I, 93  
WALDER. Methylene green, V, 358
- GNEHM, R. and KAUFLER, F. Immedial pure blue dyes, V, 379
- GOBERT. See *Kling*.
- GOBLEY. Composition of egg-yolk, VIII, 435  
of eggs of carp, VIII, 460
- GODCHOT. See *Jungfleisch*.
- GODEFFROY, R. Metatungstic acid as reagent for alkaloids, VI, 188  
Silicotungstic acid, use of, as a precipitant for alkaloids, VI, 188; IX, 479
- GÖCKEL. Caffeine, solubility of, VI, 583  
Specific gravity, calculation of, from Baumé hydrometers, I, 11  
Theobromine, solubility of, VI, 592  
See *Trillisch*.
- GOELDNER. Formula for gelsemine, VII, 32
- GÖRNER. See *Rosenthaler*.
- GOLBERG. Iodine value of olive oil, II, 113
- GOLDBERG, E. Extraction of leather, IX, 413
- GOLDMANN and BAUMANN. Detection and isolation of cystin in urine, VII, 245
- GOLDSCHMIDT and CONSTAM. Preparation of pyridine bases, VI, 131
- GOLDSMITH. See *Farrell*.
- GOLSE. Estimation of benzaldehyde, IX, 287
- GOMBERG. Estimation of caffeine, VI, 612  
Perhaloids of caffeine, VI, 589  
and CONE. Constitution of triphenylchloromethane and analogous compounds, V, 238
- GONNFRMANN, M. Estimation of glycocoll, VII, 211
- GOODWIN. See *Robinson*.
- GOPPELSRÖDER. Formation of perthiocyanogen by the electrolysis of potassium thiocyanate, VII, 546
- GOPPELSRÖDER, F. Examination of the capillary attraction of dyes, V, 442
- GORDAN. Percentage of fat in separator slime, VIII, 184
- GORDIN. Aconite, assay of, VI, 281  
Alkaloids, estimation of, by means of iodine, VI, 190  
Berberine, VI, 552  
detection of, in plants, VI, 555  
estimation of, VI, 558  
purification of, VI, 553  
Coniine, assay of, in hemlock, VI, 222  
Mayer's reagent, use of, in the estimation of alkaloids, VI, 195  
Morphine, estimation of, VI, 433  
Nux vomica, estimation of the alkaloids in, VI, 472  
See *Prescott*.  
and PRESCOTT. Estimation of berberine in roots, VI, 556  
Estimation of hydrastine, VI, 569, 570
- GORE. Composition of grape juices, IX, 114  
Estimation of volatile acids in wines and vinegars, IX, 92
- GORIS. Phenolic substances in kola seeds, VI, 682  
See *Perrot*.  
and CHEVALIER. Kolatgin in kola seeds, VI, 682
- VON GORKOM. Yield of alkaloids in plants, VI, 170
- GORNI. Extraction of wines by carbon disulphide, III, 477
- GORSLIN and COOKE.  $\beta$ -Hydroxybutyric acid, estimation of, IX, 578
- GORTER. Caffeine, estimation of, IX, 526  
Caffetannic acid, VI, 646  
Chlorogenic acid, detection of, IX, 531  
Coffearine and trigonellin, identity of, IX, 533  
India-rubber latex, analysis of, IX, 320  
Trigonelline in coffee, VI, 648
- GORUP-BESANEZ. Proportion of silica in hair, VIII, 676
- GOSSE. See *Wallach*.
- GOTTFRIED. See *Kapeller*.
- GOTTLIEB. Estimation of urea by precipitation as the oxalate, VII, 297  
and STEPPUHN. Isolation of morphine from animal matter, VI, 438
- GOUPÉL. Ammonium hydrogen malate in tobacco leaves, VI, 248
- GOURMAND. See *Boussault*.
- GOWERS and HALDANE. Hæmoglobinometer VIII, 562
- GOWING-SCOPES. Citric acid, estimation of, IX, 112  
Fat, extraction of, IX, 117  
Halogen values of fatty acids, IX, 121  
Tartaric acid, estimation of, in fruit juices, IX, 107
- GRABOWSKI. Phlobaphenes from tannins of oak, ratanhia and tormentilla, V, 12
- GRÄBE. Melting point of phthalic acid, III, 543
- GRÄBE. Boiling point of phthalic anhydride and phthalimide, III, 544  
and EICHENGRÜN. Effect of heat on salicylic acid, III, 475

- GRAEBE, C.** Analysis of purr e, VII, 395  
**GRAEFE.** Iodine value of olefines, IX, 233  
**GRAF.** Cacao butter, composition of, II, 177  
     Caffetannic acid, VI, 645  
     Pepper, analysis of, VII, 64  
**GRAF, B.** Composition of dammar resin, IV, 61  
**GRAFE.** Caff ol in coffee, IX, 531  
**GRAHAM, CHAS.** Specific gravity of solutions of malt extract, I, 289  
     **HOFMANN and REDWOOD.** Specific gravity of sugar solutions, I, 289  
     Original specific gravity of beer wort, I, 151  
     **STENHOUSE and CAMPBELL.** Aqueous extract of coffee, VI, 658  
     Determination of the adulterants in coffee, VI, 676  
**GRAHAM, SMITH and SANGER.** Detection of blood stains on leather, VIII, 573  
     Precipitation test for blood, VIII, 578  
**GRANDIS.** Gerontine, VII, 353  
     Isomers of cadaverine, VII, 349  
**GRANDMOUGIN and LANG.** Flavosine, V, 364  
     Hexamethyltriaminophenylacridine, V, 370  
     **WALDER.** Methylene green, V, 358  
**GRANDVAL and LAJOUX.** Preparation of phenol 2 : 4-disulphonic acid, III, 397  
     and **VALSER.** Adulteration of oleic acid with linseed oil acids, II, 409  
     Test for sparteine, VI, 235  
**GRANIER.** Colour reactions for digitoxin and digitalin, VII, 120  
**GRASSER.** Apparatus for tannin extraction, V, 57  
     Estimation of free acid in tan-liquors, V, 98  
**GRASSER, G.** Neradol D, IX, 409  
**GRASSLER.** Estimation of tannins, V, 93  
**GRAY.** See *Sherman*.  
**GRAY, A.** Guayule rubber, IV, 107  
**GRAY, S.** Stirrer for Abel's closed oil tester, III, 124  
**GRAY, T. T.** Lubricating oils, carbon residue test for, IX, 254  
**GREAVES.** Estimation of gliadin in flour, VIII, 101  
**GREEN.** Eosins, reduction of, V, 297  
     Wines, foreign colouring matters in, I, 177  
     and **FRANK.** Identification of vat dyes, V, 534  
**GARDNER, LLOYD and FRANK.** Indigo, IX, 427  
     and **PERKIN.** Phenolphthalein as an indicator, V, 265  
     **WINDRIDGE.** Detection of bismuth nitrate in bismuth salicylate, III, 490  
     **WOODHEAD.** Constitution of aniline black, V, 316  
**GREEN, A. G.** Amino-ditolyl-*p*-toluquinonediimine, VI, 66  
     Aniline black, constitution of, V, 313  
     Colouring matters, classification of, V, 267, 460  
     Azines, oxazines and thiazines, formul e for, V, 318, 319  
     Dyestuffs, artificial, analysis of, V, 266  
     *p*-Toluidine, effect of heating, with sulphur, V, 371  
     and **KING, P. E.** Phenolphthalein, constitution of, III, 550; V, 263  
**GREEN, A. G., YEOMAN, H. and JONES, J. R.** Identification of dyestuffs on animal fibres, V, 489  
**GREENHAIGH, N.** See *H. A. Tempney*.  
**GREENISH.** Microscopic identification of starches, I, 411, 414  
     Myrosin in black mustard seeds, VII, 106  
**GREENISH, H. G.** Cape tea, VI, 602  
     Ipecacuanha, VII, 49  
     root, VII, 43, 44  
     Pepper and its adulterants, microscopical examination of, VII, 59  
     Nitric acid test for myrrh, IV, 99  
**GREENLEE.** Composition of eggs, VIII, 440  
     Loss of moisture of eggs during cold storage, VIII, 441  
     See *Pennington*.  
**GREENWALD.** Creatine and creatinine, estimation of, IX, 568  
**GREGOR, G.** Determination of the methoxyl number of essential oils, IV, 240, 241  
     Methoxyl values of resins, IV, 10, 15  
     and **BAMBERGER.** Methoxyl number of ammoniacum, IV, 92  
     of asafoetida, IV, 95  
     of dragon's blood resin, IV, 64  
     of guaiacum, IV, 66  
     for myrrh, IV, 102  
**GREGORY, J. C.** See *F. W. Richardson*.  
**GREIFENHAGEN, K NIG and SCHOLL.** Separation of gelatin from digestion products, VIII, 485  
**GRESHOFF.** Alkaloids from the composit e, VI, 168  
     Carpaine, VII, 1  
     Hydrocyanic acid, occurrence of, in tropical plants, VII, 462  
     Sophorine and cytosine, identity of, VII, 15  
**GRETHE.** See *Lifschutz*.  
**GRIESHEIM-ELEKTRON Co.** Corioflavines, V, 365  
**GRIESS and HARROW.** Cholin from hops, VII, 173  
**GRIGAUT.** Estimation of cholesterol, IX, 226  
**GRIGGI, C.** Reaction of gallotannic acid, V, 21  
     Test for gallic acid with potassium cyanide, III, 529  
**GRILLO and SCHROEDER.** Manufacture of glue, VIII, 602  
**GRIMALDI.** See *Campani*.  
**GRIMAUD.** See *Lauth*.  
     and **ARNOLD.** Conversion of cupreine into quinine, VI, 502  
**GRIMME.** Extraction of fat, IX, 117  
     Hardened marine animal oils, IX, 123  
     Mustard oil, IX, 134  
**GRIMSHAW, H.** Assay of acetate of lime, I, 507  
**GRIMWOOD.** Analysis of glycerol, IX, 213  
**GRINDLEY.** Beef, lean, composition of, VIII, 305  
     Creatinine, estimation of, in meat extracts, VIII, 410, 411  
     Meat, cold water extract of, VIII, 299  
     See *Emmet*.  
     and **WOODS.** Creatinine and creatine in beef extracts, VIII, 411  
     Estimation of creatinine, VIII, 397  
**GRISPO.** Saffron, V, 420

- GRITTNER, A. Test for rosin oil, IV, 43  
 DE GROBERT. See *Pellet*.  
 GRÖNEWOLD. Barbaloina, VII, 139  
 GROSJEAN. Difficulties with slow filtering material, I, 547  
     Table showing specific gravity, free acid, and organic acid in citric acid juices, II, 560  
     See *Jorissen*.  
 GROSS. See *Sherman*.  
 GROSSETESTÉ, C. Microscopic character of silk, VIII, 641  
 GROSSMANN. Comparative dyeing trials for indigotin, V, 392  
     Estimation of indigotin, V, 395  
 GROSVENOR. Assay of acetate of lime, I, 508  
 GROSZFELD. See *König*.  
 GROTHE. Distinction between wool and silk, VIII, 647  
 GROTRIAN, W. and RUNG, C. Cyanogen, detection of, spectroscopically, IX, 585  
 GROVES. Formation of monamines, VI, 3  
     See *Plimpton*.  
 GROVES, T. B. Analysis of flower of tea, VI, 601  
 GRUBE, G. and KRÜGER, J. Calcium cyanamide, estimation of, IX, 590  
 GRÜBER. *o*-Cresol, III, 313  
     Detection of ergot in flour, I, 458  
 GRÜN.  $\alpha$ -Dipalmitin, II, 397  
     and SCHACHT. Double melting points of various mixed glycerides, II, 52  
 GRUENERT, O. See *K. Fischer*.  
 GRÜNHUT. Acrolein test for glycerol, II, 453  
     Detection of glycerol in coffee berries, VI, 652  
 GRÜNHUT, L. See *W. Fresenius*.  
 GRUËSS. Oxidising enzyme in yeast, I, 213  
 GRÜSSNER. See *Benedikt, Hasura*.  
 GRÜTZNER. Estimation of the proteoclastic power of pepsin, VIII, 494  
     Rennet-enzyme, VIII, 126  
 GRUTTERINK and VAN RYN. Morphine, toxicology of, IX, 508  
 GRUSEWSKA. See *Bierry*.  
 GSCHIEDLEN. Preparation of oxyhæmoglobin, VIII, 507  
     Presence of thiocyanates in the salivary gland, VII, 543  
 GSCHWENDNER. Polarimetric estimation of starch in maize and cereals, I, 425  
 GSELL. Hydrastis extract, estimation of hydrastine and berberine in, IX, 524  
 GUARESCHI. Function of alkaloids in plants, VI, 169  
 GUARESCHI, I. Bromine, detection of, IX, 587  
 GUDEMAN, E. Estimation of sulphites in food gelatin, VIII, 617  
 GUDZENT. Iso-dynamic forms of uric acid, VII, 364  
 GÜMBEL. Determination of the Hausmann numbers of proteins, VIII, 81  
 GUENEZ. Estimation of tannins, V, 93  
 GÜNTHER. Estimation of tannins, V, 85  
 GÜNZEL. Calumba, VI, 575  
 GÜRBER. Albumin, VIII, 91  
 GUERIN. Morphine, estimation of IX, 505  
     and narcotine, solubility of in acetone and water, IX, 496  
 GUÉRIVE. See *Sabrazès*.  
 GUESLAU. See *Dupont*.  
 GUEST. See *Osborne*.  
 GUGGARI, P. B. See *F. M. Litterschied*.  
 GUGLIELMETTI and COPETTI. Estimation of glycerol in wines, I, 167  
 GUIBOURT. Analysis of gall-nuts, V, 35  
 GUIGNET. Conversion of gallic acid into benzoic acid, III, 527  
     Preparation of Turnbull's blue, VII, 526  
 GUILLAUME, GENTIL. Use of mercury solutions for the estimation of sugars, I, 337  
 GUIMARAES. See *Comy*.  
 GUISIANA, E. Tannin analysis, use of gelatin and fish glue in, IX, 606  
     Test for tannin, IX, 394  
 GULEWITSCH. Cadaverine platinichloride, VII, 348  
 GULLI. See *Berté*.  
 GULLI, S. Adulterant of bergamot oil, IV, 318  
 GULLIVER. Size of red corpuscles, VIII, 501  
 GUNTHER. Alkaloids in belladonna, VI, 313  
 GUOZDENOVIC. Iodine value for olive oil, II, 113  
 GUTH. Olein, II, 412  
     Palmitin, II, 397  
     Stearin, II, 401  
     See *Bullenberg*.  
 GUTHRIE. Solubility of trimethylamine in water, VI, 16  
 GUTTMANN. Test for explosives, III, 612  
 GUTZEIT. Increase of viscosity by the change of calcium casein into calcium paracasein, VIII, 126
- H
- VAN DER HAAR. Hydrastine, estimation of, IX, 523  
     Saponin from *polyseias nodosa*, VII, 128  
 VAN HAAREN. See *Partheil*.  
 HAARS. Formula of corydaline, VI, 205  
 HAAS. Estimation of nitrogen in organic substances containing methoxyl or ethoxyl groups, I, 59  
     Hippuric acid, detection of, IX, 570  
 DE HAAS, T. See *V. Romburgh*.  
 HABERMANN. Hydrocyanic acid in tobacco smoke, VII, 463  
 HACKFORD. See *Trotman*.  
 DE HAEN. Estimation of ferrocyanides, VII, 511  
 HAENSEL. Acaroid resin oil, IV, 17  
     Angelica oil, IV, 310  
     See *Nerking*.  
 HAENSEL, H. Specific gravity of dammar resin, IV, 61  
     Terpeneless essential oils, IV, 429  
 HÄRTEL and WILL. Pepper, analysis of, VII, 64  
     black, crude fibre in, VII, 59  
     weight of peppercorns in, VII, 58  
     estimation of ethereal oil in, VII, 63  
     of piperine in, VII, 62  
 HÄUSSLER. Test for citric acid, IX, 115

- HÄUSERMANN, C.** Preparation of pyridine bases, VI, 131
- HAFNER.** See *Kreis*.
- HAGEN.** See *Müller*.
- HAGER.** Beeswax, action of ether on, II, 243  
Benzoic acid, test for the origin of, III, 408  
Chloroform, detection of alcohol in, I, 278  
Cinchona barks, estimation of alkaloids in, VI, 489  
Copaiba balsam, detection of sassafras oil in, IV, 82  
Dextrose, estimation of, by a solution of mercuric acetate, I, 337  
Fats, specific gravity of, I, 15; II, 48  
Guaiacum, detection of colophony in, IV, 66  
Opium, tests for the purity of, VI, 417  
Picric acid test for alkaloids, VI, 185
- HAGER, H.** Estimation of aloes in mixtures, VII, 151
- HAHN.** "Endoenzymes" in yeast, I, 211  
See *Böcker*.  
and **GERET.** Properties of yeast-endotryptase, I, 212
- HAIG, A.** Effect of the administration of acid on the amount of uric acid excreted, VII, 380
- HAKE and LEWIS.** Sulphuric esters of guncotton, III, 568
- HALBEY.** See *Tschirch*.
- HALDANE.** Carbon monoxide in blood, symptoms caused by, VIII, 535  
Carboxyhæmoglobin, estimation of, in blood, VIII, 532  
Cyanhæmoglobin, VIII, 537  
Hæmoglobin, affinity of, for carbon monoxide, VIII, 530  
Oxyhæmoglobin, conversion of, to methæmoglobin, VIII, 540  
Poisoning by nitrites, VIII, 537  
Saltpetre, action of, in the curing of meat, VIII, 364  
See *Gowers*.
- HALENKE and MÖSLINGER.** Estimation of tartaric acid and tartrates in wines, I, 177
- HALL, MARSHALL.** Physiologic test for strychnine, VI, 454
- HALLE, LOEWENSTEIN and PRIBRAM.** Ninhydrin test for amino-groups, IX, 560
- HALLER.** Alcohols, estimation of, in essential oils, IV, 230  
Borneol, racemoid modification of, IV, 278  
Camphor, formation of, from camphoric acid, IV, 203  
racemic, IV, 194  
Fats, analysis of, by alcoholysis, II, 13  
Linseed and castor oils, examination of, IX, 118  
oil, alcoholysis of, IX, 184  
composition of, II, 330  
Rosemary oil, composition of, IV, 390  
and **MICHEL.** Removal of thiophen from benzene, III, 211
- YOUSSEUFIAN.** Composition of coconut oil, II, 13, 188
- HALLIBURTON.** Globulins, VIII, 91  
Myosin and myogen, VIII, 92
- HALLIBURTON, W. D.** Structure of human muscle, VIII, 278
- HALLOPEAU, L. A.** Estimation of peptones, VIII, 396
- HALPHEN.** Benzoic acid, detection of, III, 410; IX, 280  
Cacao butter, substitute, detection of, IX, 150  
Linseed oil, detection of, in walnut oil, II, 353  
insoluble bromides from, II, 337  
Rosin oil, detection of, in the presence of mineral oil, IV, 44  
See *Riche*.
- HALS.** Analyses of Norwegian cheeses, VIII, 253
- HALTZ.** See *Marchwald*.
- HAMBLY.** See *Walker*.
- HAMMARSTEN.** Casein, solubility of, in di- and tri-phosphates, VIII, 124  
Caseinogen, VIII, 91  
Fibrinoglobulin, VIII, 91  
Fish, reducing substances in, VIII, 460  
Mucin, analysis of, VIII, 628  
Mucins, VIII, 92  
 $\beta$ -nucleoprotein, VIII, 92  
Rennet coagulation, compounds which retard, VIII, 130  
Rennet-enzyme, VIII, 126, 128  
and **MALY.** Presence of casein in milk as a compound with calcium phosphate, VIII, 119
- HAMMER.** See *Reynold*.
- HAMMERSCHLAG.** Specific gravity of defibrinated blood, VIII, 498  
See *Sherman*.
- HAMOR.** See *Baskerville*.
- HAMPSHIRE and PRATT.** Quinine formate, IX, 518
- HANAUSEK.** Coffee free from caffeine, VI, 657
- HANBURY.** Mineral adulteration of saffron, V, 419
- HANDOVSKY.** See *Pauli*.
- HANENSCHILD.** Tensile strength and penetration of asphalt paving mixtures, III, 98
- HANN.** See *Tutin*.
- HANSEN.** Beef and mutton tallow, composition of, II, 208  
Yeast, cell wall of, I, 206  
classification of, IX, 15  
culture, I, 214, 215, 216  
microscopical examination of, I, 221  
spore formation in, I, 210  
vitality of, I, 210
- HANSEN, JESSEN.** Estimation of sugar by Bang's method, I, 335
- HANSSSEN.** Amyloid, VIII, 91
- HANTZSCH.** Constitution of oxazines, V, 341  
Structure of asines, oxazines and thiazines, V, 319  
and **OSSWALD.** Salts of pararosaniline and crystal violet, V, 239
- HANUŠ.** Cinnamic aldehyde, estimation of, III, 442; IX, 336  
occurrence of, in cinnamon, III, 441  
Butter fat, detection of coconut oil in, II, 284

- HANUŠ. Essential oils, use of semioxamizide in the estimation of aldehydes and ketones in, IV, 233  
 Hazelnut oil, composition of the fatty acids of, II, 105  
 Vanillin, estimation of, III, 517, 518  
 and STEKL. Ethyl ester value for coconut oil, II, 189
- HARCOURT. Composition of breakfast-foods, I, 464
- HARDEN. Colour test for proteins, VIII, 41  
 and NORRIS. Colour test for proteins, VIII, 41  
 THOMPSON and YOUNG. Measurement of the activity of zymase, VIII, 9
- HARDER. Estimation of vanillin, IX, 308
- HARDING. See *Frankforter, Hudson, Van Slyke*.
- HARDY. Identification of proteins by their solubilities, VIII, 76  
 Pilocarpine, VII, 51  
 See *Tarbows*.  
 and GARDINER. Separation of the total proteins from blood-serum and plasma, VIII, 53
- HARE. See *Gibbs*.
- HARGREAVES and ROUX. Microscopic test for mercury in explosives, III, 611
- HARKER. Fermentation of cane-sugar molasses, I, 357
- HARMAN. See *Briant*.
- HARNACK. See *Frerich*.  
 and MEYER. Alkaloids of jaborandi, VII, 52
- HARNACK, E. Egg albumin, VIII, 434
- DE LA HARPE. See *Reverdin*.
- HARRIES. Additive compound of ozone and india rubber, IV, 110  
 Hydrocarbon of india-rubber, IV, 107  
 See *Fischer*.  
 and JOHNSON. Synthesis of  $\alpha$ -phellandrene, IV, 171
- RIMPEL. Axchod's method for the estimation of rubber in vulcanised rubber, IV, 134  
 Estimation of pure rubber in raw rubber, IV, 110
- SCHAUWECKER. Constitution of citronellal, IV, 269  
 of citronellol, IV, 263
- HARRIS. Wheat proteins, VIII, 96  
 See *Osborne*.  
 and CLOVER. Heroin hydrochloride, IX, 500  
 OSBORNE. Identification of proteins by their solubilities, VIII, 76
- HARRISON. Bismuth salicylate, solvent for free salicylic acid in, III, 490  
 Sugars, estimation of, in condensed milk, VIII, 213  
 See *Dunstan, Richmond*.  
 and CORNELL. Ripening of cheese, VIII, 243  
 MAISCH. American storax, III, 462  
 SELF. Asafetida and ammoniacum, IX, 316  
 test for, IX, 318  
 Nicotine, estimation of, IX, 485
- HARRISON, E. F. Use of starch and potassium iodide as an indicator in Soxhlet's method of estimating sugars, I, 321
- HARROW. See *Griess*.
- HARRY, F. J. and MUMMERY, W. R. Salicylic acid, estimation of, I, 163; III, 485
- HART. Acetone, estimation of, in urine, IX, 576  
 Amino-acids formed by the hydrolysis of caseinogen, VIII, 20  
 Saffron, V, 419  
 See *Susuke, Van Slyke*.
- HART, E. B. See *E. G. Hastings*.
- HART, J. H. Fermentation of cacao beans, VI, 686
- HART, W. B. Estimation of antimony in tartar emetic, I, 553  
 Presence of copper in food gelatin, VIII, 616
- HARTLEY. Driers, II, 360
- HARTLEY, W. N. Quinonoid structure of triphenylmethane dye-stuffs, V, 238
- HARTWELL. See *Chittenden*.
- HARTWICH, C. Ipecacuanha, VII, 49  
 and HELLSTRÖM. White Peru balsam, III, 455
- HARTZ. Alkaloid from stramonium seeds, VI, 319
- HARVEY. Refractive index of almond oil, II, 102  
 of linseed oil, II, 338  
 See *Pope*.
- HARVEY, S. Estimation of salicylic acid in foods, III, 484
- HASHIDA. Distinction between morphine and pseudomorphine, VI, 437
- HASLAM. Examination of protein digests by fractional precipitation, VIII, 482  
 Precipitation of proteins by salts, VIII, 66
- HASS and HOERNSTEIN. Crude fibre in black pepper, VII, 59
- HASSOCK. Size of silk and artificial silk filaments, VIII, 663
- HASTINGS. See *Ravenel, Susuke*.
- HASTINGS, E. G., EVANS, A. C. and HART, E. B. Ripening of cheese, VIII, 245
- HATA. Estimation of the proteoclastic power of pepsin, VIII, 493
- HATCH. See *Gill*.
- HATCHER. Digitalis, IX, 546
- HATCHETT. Composition of lac-dyes, V, 424
- HATMAKER. Process for drying milk, VIII, 235
- HAUFF, J. Cresolic acid as a beating liquid in tanneries, III, 511
- HAUSER, O. See *A. Lewite*.
- HAUTH. Separation of Hesse's phytosterol into its constituents, II, 493  
 See *Windsus*.
- HAWK. See *Bergeim, Wills*.  
 and GIES. Chondroproteins, VIII, 91
- HAWK, P. B. Animal acids, IX, 569
- HAWLEY. See *Elsdon*.
- HAWLEY, L. F. Wood turpentine, IX, 381
- HAY. Bile acids, detection of, IX, 578
- HAYDUCK. Hops, bitter substances and resins of, VII, 165  
 Yeast, IX, 17  
 determination of the fermenting power of, I, 223  
 and BULLE. Drying of yeast, IX, 16
- HAYWOOD, J. K. and SMITH, B. H. Estimation of formaldehyde by the hydrogen peroxide method, I, 261



- HAZARD.** See *Bierry*.
- HAZEWINKEL.** Indican, v, 385
- HAZURA.** Detection of linseed oil acids in commercial oleic acid, II, 409  
See *Bauer*.
- and **GRÜSSNER.** Hempseed oil, composition of, II, 150  
Linseed oil, composition of, II, 330  
Poppyseed oil, liquid fatty acids from, II, 152  
Walnut oil, composition of, II, 157
- HEADLAND.** Poisoning by aconite, VI, 284
- HEANEY.** California bay oil, IV, 316
- HEATON and VASEY.** Analysis of peptones, VIII, 396
- HEAVEN.** See *Wilson*.
- HECKEL and SCHLAGDENHAUFFEN.** Analysis of kola, VI, 680
- HECZKO.** Estimation of tartaric acid, IX, 104
- HEERMAN, P.** Estimation of small quantities of wool in cotton materials, IX, 623
- HEERMANN.** Silk-weighting, VIII, 654, 661
- HEFELMANN.** Estimation of saccharin, III, 433
- HEFELMANN, R.** Analysis of resinate driers, IV, 35
- HEGLAND.** Gravimetric estimation of hydrastine, VI, 570
- HEHNER.** Beef tea, analysis of, VIII, 396  
Beeswax, estimation of cerotic acid in II, 246, 247, 248  
Brandy, analysis of, I, 200  
Bromine value for oils and fats, gravimetric method for the determination of the, II, 27  
Candle mixtures, analysis of, II, 262  
Glycerol, estimation of, II, 460, 467  
volatilisation of, II, 450  
Meat extracts, composition of, VIII, 397, 420  
estimation of creatinine in, VIII, 411  
Milk, calculations for the analysis of, VIII, 163  
detection of fluorides in, in the presence of boron compounds, VIII, 190  
of formaldehyde in, VIII, 171  
test for presence of formaldehyde, I, 259  
Milk-sugar, specific gravity of solutions of, I, 289  
Phenol test for formaldehyde, I, 259  
Spermaceti, commercial, II, 275  
Sugars, estimation of, with Pavy's solution I, 332  
Tin in canned meat, VIII, 338  
Turpentine oil, bromine thermal test for, IV, 424  
and **HÜBL.** Creotic acid in carnaúba wax, II, 270
- MITCHELL.** Almond oil, composition of, II, 102  
Beef fat, crystallisation of, II, 321, 322  
Bromine thermal method for the determination of the unsaturation of fats, II, 60  
Chinese vegetable tallow, composition of, II, 181  
wood oil, hexabromide test for, IX, 143  
Coconut oil, composition of, II, 188
- HEHNER.** Insoluble bromide test for the purity of oils, II, 28  
Japan wax, fatty acids from, II, 193  
Lard, proportion of stearin in, II, 318  
Linolenic acid, specific gravity of, II, 352  
Linseed oil, insoluble bromides from, II, 336  
hexabromide test for, IX, 189  
Mustard-husk oil, brominated glyceride from, II, 120  
Palmitic acid, solubility of, in alcohol, II, 396  
Poppyseed oil, II, 152  
Stearic acid, absence of, in olive oil, II, 108  
in butter fat, II, 280  
in cacao butter, II, 177  
estimation of, in a mixture of fatty acids, II, 393  
in tallow, II, 208  
Walnut oil, adulteration of, II, 159  
iodine value of the mixed fatty acids from, II, 158  
Whale oil, composition of, II, 229
- RICHMOND.** Calculations for the analysis of milk, VIII, 163
- SKETCHLEY, N. P.** Estimation of fibre in cocoa, VI, 708  
of penrosans in coffee, VI, 645
- VON DER HEIDE.** Extraction apparatus for the estimation of lactic acid, VII, 437  
and **JAKOB.** Benzoic acid, detection of, VIII, 173; IX, 280  
Cinnamic acid, detection of, in urine, IX, 291  
Salicylic acid, test for, IX, 301
- VON DER HEIDE, C. and STEINER, H.** Estimation of succinic acid in wine, IX, 97
- HEIDELBERG.** See *Bernegan*.
- HEIDUSCHKA and RHEINBERGER.** Trichlorotri-iodolinolenic acid, IX, 185
- HEIKEL.** Acetone, commercial, I, 109  
Mayer's reagent, use of, for the estimation of alkaloids, VI, 192  
Morphine, estimation of, VI, 384
- HEILBRON.** See *Henderson*.
- HEIM.** Hydrastine, VI, 564
- HEINE and Co.** Composition of clove oil, IV, 330
- HEINRICH.** Estimation of glucose in the presence of sucrose by Sachse's mercuric solution, I, 338
- HEINTZ.** Melting point of lead palmitate, II, 399  
Separation of the stearic acid series of acids, II, 382, 384, 386  
and **LIMPRICH.** Estimation of salicylic acid, IX, 302
- HEINTZ, A.** Estimation of rubber in vulcanised rubber, IV, 136
- HEINZ.** Pharmacology of aconite bases, VI, 287
- HEINZERLING and PAHL.** Influence of various organic and inorganic admixtures in rubber, IV, 119
- HEISCH.** Analysis of cocoa nibs, VI, 689  
of pepper, VII, 63
- HEISE.** Composition of Goa butter, II, 182  
Presence of mixed glycerides in fats, II, 8  
See *Rost*.



- HELPERICH.** See *Fischer*.
- HELTERS.** Apparatus for determining the gas value of an oil, III, 139
- HELL and MEIDINGER.** Wallachian petroleum, III, 44
- ROCKENBACH.** Non-basic constituents of aniline and toluidine tailings, VI, 76
- SCHOOP.**  $\beta$ -Toluylene-diamine, VI, 107
- HELLER.** Constitution of fluorescein, V, 292
- HELLER, G.** Purification of gallein, V, 299
- HELM and POTONIC.** Varieties of amber, IV, 18
- HEMPER.** Apparatus for fractional distillation, I, 21
- Estimation of gaseous olefines, III, 4
- and **KAHL.** Volumetric estimation of hydrogen phosphide in acetylene, III, 10
- HENDERSON and Heilbron.** Distinction between borneol and isoborneol IX, 342
- Adulteration of caraway oil with castor oil, IV, 325
- Alkaloids in belladonna, VI, 313
- Henneberg.** Yeast Glycogen, I, 209; IX, 16
- protein, IX, 16
- Henninger.** Melting point of glycerol, II, 447
- See *LeBel*.
- HENRI, VICTOR.** Electrocathaphoresis experiments with proteins, VIII, 89
- Size of india-rubber globules, IV, 105
- HENRIQUES, R.** Beeswax, detection of ceresin or rosin in, II, 257
- determination of the saponification value of, II, 252
- Benzenes, separation of, from petroleum spirit, III, 241
- Cocaine, test for, VI, 325
- Colophony, absence of resin esters in, IV, 25
- Oils and fats, cold saponification of, II, 16
- Triglycerides, saponification of, with alkali, II, 13
- Rubber, acetone extraction of, IV, 126
- estimation of unsaponifiable oils in, IV, 125
- goods, estimation of carbon in, IV, 137
- percentage of resin in, IV, 111
- regeneration of, IV, 133
- substitutes, IV, 148, 149
- vulcanised, analysis of, IV, 129, 730
- estimation of sulphur in, IV, 139
- See *Sørensen*.
- GJALDBÆK.** Digestion products, hydrolysis of, VIII, 489
- Plasteins, VIII, 495
- Protein digests, preparation of, VIII, 481
- Proteins, estimation of the reactive carboxylic acid groups in, VIII, 90
- KÜNNE.** Presence of mixed glycerides in fats, II, 8
- HENRY.** Cyanogen, preparation of, from oxamide, VII, 454
- Lard oil, solidification of, II, 197
- Linseed cake, composition of, II, 326
- See *Dunstan*.
- and **AULD.** Hydrogen cyanide from cyanogenetic glucosides, I, 392; VII, 101
- HENRY, THOMAS A.** Callitrolic and pimaric acids, IV, 5
- HENRY, THOMAS A.** Vegetable alkaloids, VI, 167; IX, 477
- HENSLER and HERDE.** Estimation of paraffin in crude anthracene, III, 281
- HENZE.** Gorgonin, VIII, 91
- Hæmocyannin, VIII, 559
- Spongosterol, VIII, 673
- from suberites domuncula, II, 486
- HENZOG and ROSENBERG.** Analysis of leather, V, 105
- HENZOLD.** Estimation of gelatin in gums, VIII, 593
- HEPBURN.** See *Pennington*.
- HEPP.** See *Fischer*.
- HERBIG.** Turkey-red oil, estimation of fatty-sulphuric acid in, II, 170
- the total fatty matter in, II, 169
- separation of, IX, 145
- Wool-fat, estimation of unsaponifiable matter in, II, 500
- extraction of, by ether, II, 497
- saponification of, II, 499
- HERDE.** See *Hensler*.
- HERETH.** Use of Mayers' reagent for the estimation of alkaloids, VI, 195
- HERFELDT and STUTZER.** Roasting of coffee, VI, 648
- HÉRISSEY.** Estimation of benzaldehyde, III, 419
- HERLANT.** Determination of the electrical conductivity of oils and fats, II, 45
- HERMANN.** Morphine, biological test for, IX, 498
- Presence of bromoform in commercial bromine, I, 282
- HERMANNS.** See *Windans*.
- VAN HERNERDEN.** Action of rennet-enzyme, VIII, 129
- HERON.** Estimation of tannin in hops, VII, 188
- See *Brown*.
- HERR, V. F.** Use of methylal in hydrocarbon analysis, IX, 236
- HERTEL, J.** Extraction of colchicine, VII, 9
- HERTING.** Estimation of cyanates, VII, 487, 541
- HERTKORN.** Action of tung oil on the skin, II, 157
- Break test for linseed oil, IX, 186
- HERTMANN.** Zeisel and Panto's method for the estimation of glycerol, II, 463
- HERTWIG, R.** Occurrence of hæmoglobin, VIII, 506
- HERZ, N.** Sodium zinc cyanide, IX, 587
- HERZFELD.** Honey, artificial, I, 386
- Invert sugar and cane sugar, specific gravity of corresponding solutions of, I, 295
- Milk sugar, action of Fehling's solution on, I, 362
- Sugars, estimation of, IX, 24
- Tryptophane, estimation of, IX, 563
- and **REISCHAUER.** Saccharin, detection of, IX, 289
- estimation of, in wines, I, 176
- HERZFELD, H.** Estimation of petroleum naphtha in turpentine oil, IV, 416
- HERZIG.** Determination of the methoxyl numbers of essential oils, IV, 240
- and **MEYER.** Estimation of methoxyl groups in alkaloids, VI, 203
- Methoxyl number of essential oils, IV, 241

- HERZOG.** Assay of benzaldehyde, IX, 288  
Cellulose acetate filaments, VIII, 668  
and **MEIER.** Estimation of oxydase, VIII, 14  
**POLOTZKY.** Estimation of oxydases, VIII, 14  
**HESS and PRESCOTT.** Separation of vanillin and coumarin, III, 519  
**HESSE.** Alkaloids from *Remijia purdieana* and *cinchona pelletierana* barks, VI, 547  
*β*-Amyrin, II, 488  
Berbamine, VI, 563  
Chrysophanic acid, melting point of, V, 227  
Cinchona alkaloids, tests for, VI, 505, 506  
Cinchonidine sulphate, detection of cinchonine and quinidine sulphates in, VI, 539  
Coca, amorphous bases of, VI, 343  
Cocamine, VI, 340  
Fat, estimation of, in butter, II, 307  
Hydroquinine, VI, 533  
Hyoscyamine in *Mandragora vernalis*, VI, 290  
Ipecamine and hydro-ipecamine, IX, 542  
Mandragorine, VI, 301  
Opium bases, colour reactions of, VI, 367, 368  
separation of, VI, 372  
Oxyacanthine, melting point of, VI, 526  
Papaverine, reaction of concentrated sulphuric acid with, VI, 199  
Phytosterol from *aristolochia argentina*, II, 485  
from calabar beans, II, 484, 485  
Pseudo-hyoscyamine in *Mandragora vernalis*, VI, 298  
Pseudomorphine, constitution of, VI, 357  
Quinine, VI, 508  
chromate test for, VI, 514  
sulphate, VI, 515  
detection of other alkaloids in commercial, VI, 523  
of cinchonine in, VI, 525  
modification of Kerner's test for, VI, 520  
and **ZMITSCHEL.** Estimation of methyanthranilate in essential oils, IV, 363  
Orange-flower oil, IV, 367  
**HESSE, B. C.** Coal-tar colours, in foods, IX, 449  
**HETT.** See *Ahrens.*  
**HEUMANN.** Synthesis of indigo, V, 390  
**HEUT.** Estimation of coniine alkaloids, VI, 220  
**HEVYFELD.** Pyrrole and indole, distinction between, IX, 476  
**HEWITT.** Fluorescein, V, 287  
Phenosafranine, V, 322  
Potable spirits, estimation of acids and esters in, I, 196  
furfural in, I, 197  
and **TERVET.** Salts of fluorescein, V, 291  
**WOODFORDE.** Substitution derivatives of fluorescein, V, 293  
**HEWITT, G. T.** Dyestuffs of groups VI to XII, V, 231  
**VON HEYDEN.** Disinfectants, soluble, preparation of, III, 332  
Saccharin, preparation of, III, 428  
purification of, III, 429  
Sodium antimony lactate and sodium calcium antimony lactate, VII, 447  
**HEYL.** Assay of benzaldehyde, IX, 288  
See *Osborne.*  
**HIBBERT.** See *Gladstone, Knecht, Michael.*  
**HIEPE.** See *Schmitt.*  
**HILDEBRAND.** See *Tschirch.*  
**HILDEBRAND, K.** Composition of acaroid resins, IV, 16  
**HILGARD.** Composition of rock-asphalt, III, 61  
**HILGER.** Cocoa-red, formation of, VI, 699  
Coffee berries, detection of sugar glazing in, VI, 652  
Columbin, extraction of, VI, 576  
and **JUCKENACK.** Caffeine, estimation of, in tea, VI, 608  
Fat values of coffee, VI, 647  
Roasting of coffee, VI, 648  
**TAMBA.** Detection of hydrocyanic acid, VII, 480  
**TRETZEL.** Boheic acid in tea, VI, 599  
**HILL.** Alkaloids, salts of, VI, 185  
Cinnamon oil, detection of adulteration of, IX, 293  
specific gravity of, IX, 356  
Tartaric acid, detection of, in citric acid, IX, 114  
and **COCKING.** Analysis of liquid storax, IX, 298  
**HILL, A.** Estimation of tannin in tea, V, 67  
**HILL, A. V.** See *Barcroft.*  
**HILL, C. A.** Test for lead in tartaric acid, IX, 101  
**HILL, CROFT.** See *Gamgee.*  
**HILL, WALDEMAR.** Estimation of alkaloids in cinchona bark, VI, 489  
**HILLE, W.** Estimation of quinine, VI, 526  
**HILLER.** See *Meissl.*  
**HILLYER.** Estimation of benzoic acid in ketchups, IX, 285  
**HILTNER, R. S.** Estimation of citral, IX, 337  
**HINKEL.** Detection of methyl alcohol, I, 90  
and **SHERMAN.** Detection of dextrose by Barfoed's reagent, I, 333  
**HINKS.** Benzoic acid in milk, IX, 162  
detection of, IX, 281  
estimation of, IX, 284  
Cheese coatings, VIII, 249  
**HINRICH.** See *Schönfeld.*  
**HINRICHSEN.** India-rubber, estimation of, IX, 321  
resins accompanying, IX, 320  
vulcanised, analysis of, IV, 132  
See *Marcusson.*  
and **MARCUSSON.** Evidence of raw rubber in a sample of vulcanised rubber by its optical activity, IV, 125  
**HINRICHSEN, F. W.** Inks, writing, estimation of tannin in, IX, 468  
**HINSBERG.** Separation of amines, VI, 4  
and **KESSLER.** Separation of amines, VI, 4  
**ROOS.** Cholesterol of yeast, II, 488  
**HINSDALE.** Tincture of opium, VI, 429  
**HINSDALE, S. T.** Estimation of tannin in bark, V, 94  
**HIROHASHI.** Digitalis, IX, 546  
**HIRSCHEL.** Separation of beeswax from honey, II, 242

- HIRSCHSOHN.** Ammoniacum, iv, 91  
 Asafoetida, iv, 94  
 Colophony, detection of, in dammar resin, iv, 62  
   in oil of cassia, iii, 446  
   in Tolu balsam, iii, 460  
 Dammar resin, solubility of, iv, 61  
 Distinction between methylacetanilide, acetanilide and phenacetin, vi, 87  
 Guaiacum, test for the purity of, iv, 66  
 Gurjun balsam, iv, 88  
 Myrrh and bdellium, iv, 100  
 Oil of cinnamon, iii, 443  
 Turpentine, test for, in Venice turpentine, iv, 79
- HIRST.** See *Procter*.
- HIRT.** See *Schönfeld*.
- HJELT.** See *Aschan*.
- HLASIWETZ.** Melting point of protocathechuic acid, iii, 512  
 Oil of asafoetida, iv, 95
- HOAGLAND.** Action of saltpetre in the curing of meat, viii, 364
- HOCK.** See *Traub*.
- HODGKIN.** See *Howard*.
- HODGKINSON and SORBY.** Analysis of black pigment from feathers, viii, 679
- HODGKINSON, W. R. E.** Hydrazine nitrate, ix, 469
- HODGSON.** Moisture in coffee, ix, 530  
 See *Gardner, Russell*.
- HODGSON, E. H.** Estimation of sulphur in asphalt, iii, 85
- VON HÖHNEL.** Microscopical character of raw silk, viii, 641
- HOENIG.** Estimation of indigotin by extraction with aniline, v, 392
- HÖRMANN.** See *König*.
- HOERNSTEIN.** See *Hass*.
- HOFFBAUER.** See *Tschirch*.
- HOFFMAN.** Determination of the water in lubricating greases, iii, 179  
 Ergot, detection of, in flour, vii, 24  
 See *Paessler*.
- LAROCHE and Co.** Derivatives of atropine and hyoscyamine, ix, 490  
 Nitroprussic acid, preparation of, vii, 530
- HOFFMANN, E.** Test for phenols with Millon's reagent, iii, 297
- HOFFMANN, J. H.** Estimation of water in starch, i, 426
- HOFFMANN, K. A.** Triphenylcarbinol and analogous compounds, perchlorates of, v, 238
- HOFFMEISTER.** Estimation of benzaldehyde, ix, 288
- HOFMANN.** Amines, separation, of, vi, 5  
 Hypoxanthine, percentage of, in flesh, viii, 289  
 Muscle, Composition of, viii, 278  
 Tests for antipyrine, tolypyrine, amino-antipyrine and pyrimidone, vi, 47  
 See *Graham, Gildemeister, Robertson*.
- and **KÜSPERT.** Estimation of hydrazine, vi, 27
- LADENBURG.** Exhaustive methylation of piperidine, vi, 205
- HOFMANN, A. W.** Caffeine and tannin in maté, vi, 642  
 Chloroform, detection of, in the presence of large quantities of alcohol, i, 274  
 Crude wood-tar creosote, composition of the less volatile fractions of, iii, 352  
 Ethylamine, preparation of, vi, 20  
 Ethylene bromide, action of ammonia on, vii, 198  
 Methylamine, preparation of, vi, 13  
 Phenylbensthiazole, v, 371  
 Pyridine bases, test for, vi, 129
- HOFMEISTER.** Precipitation of proteins by salts, viii, 65
- HOHENADEL.** See *Tschirch*.
- VON HOHENHAUSEN, J.** Commercial benzol, distillation of, iii, 239  
 estimation of true benzene and its homologues in, iii, 229
- HOLDE.** Asphaltic compounds and hydrocarbon oils, separation of, ix, 231  
 Lime-soap greases, influence of the presence of water on, iii, 180  
 Lubricating greases, determination of the water in, iii, 179  
 oils, classification of, iii, 172  
 detection of caoutchouc in, iii, 171  
 test for, iii, 170  
 Oils, estimation of the hard paraffin scale in, iii, 82  
 Olive oil, composition of, ii, 107  
 Palm oil, composition of, ii, 183  
 Petroleum spirit, detection of benzene in, iii, 241  
 Rape oil, solidifying point of, ii, 123  
 Resinate driers, estimation of free resin acid in, iv, 35  
 Rosin oil, test for, iv, 43
- and **MARCUSON.** Estimation of colophony in soap, iv, 30  
 Unsaponifiable matter in colophony, iv, 27
- STANGE.** Isolation of oleo-dimargarin from olive oil, ii, 107  
 Neatsfoot oil, ii, 201
- ÜBBELOHDE and MARCUSON.** Fatty acids from lard, ii, 389
- and **WINTERFELD.** Estimation of crude benzene in alcohol, i, 113
- HOLDE, D.** Estimation of asphaltic matters in crude petroleum, iii, 54  
 Use of water and alcohol as a solvent for soap, ix, 205
- HOLDE, H.** Detection of mineral oil in rosin oil, iv, 45
- HOLDEN.** Destruction between direct and developed blacks, ix, 419
- HOLLAND.** Acetyl value for fats, ix, 121
- HOLLEMAN.** Separation of tartaric, mesotartaric and racemic acids, i, 550
- HOLLEMAN, A. P.** Estimation of impurities in o-toluidine, and o-nitrotoluene, vi, 70
- HOLLEY and LADD.** Cottonseed oil as a substitute for linseed oil, ii, 329
- HOLMES.** Aconite, root of *Imperatoria ostruthium* as an adulterant of, vi, 254

- HOLMES.** Aloes, preparation of, VII, 137  
Japanese peppermint plant, IX, 371  
Sponges, natural history of, VIII, 672  
See *Proctor, Thorpe*.
- HOLMES, E. J.** Ipecacuanhas of English commerce, VII, 49
- HOLMES, E. M.** Bay oil, IV, 314  
Belladonna roots, analysis of, VI, 311  
Cativo balsam, IV, 90  
Cinchona alkaloids, VI, 484  
Genus pelargonium, IX, 362  
Ipecacuanha, commercial varieties of, VII, 37  
Rosin spirit, composition of, IV, 38
- HOLMES, F. G.** Twisting and melting point of pitch, III, 30
- VON HOLST.** Mucin from synovial fluid, VIII, 92
- HOLTZENDORFF.** Separation of the coal-tar colours used in meat products, VIII, 387
- HONCAMP.** Lupine flakes, IX, 482
- HOOKE, S. C.** Test for pyrogallol, III, 537  
Use of carbasol as a colorimetric test for nitrates in water, III, 272
- HOOPER.** Ghedda wax, II, 268  
Indian rice, analyses of, VIII, 107  
wax, II, 269  
Ipecacuanha, percentage of alkaloids in, VII, 48  
Quinine sulphate, optical assay of, VI, 525
- HOOPER, D.** Cinchona barks, alkaloids in, VI, 484  
ash of, VI, 481  
Tannin, percentage of, in tannin-yielding materials, V, 33
- HOOPER, E. F.** Coal-tar, analyses of, III, 27  
Coke-oven tar, analyses of, III, 34
- HOPE, C.** Estimation of free alkali in soap, II, 437
- HOPKINS.** Devot's method for the estimation of proteins, modification of, VIII, 56  
Egg-albumin, crystalline, preparation of, VIII, 67  
Maize oil, solidifying point of, II, 140  
Uric acid, estimation of, VII, 370, 372  
See *Willcock*.
- and **BROOK.** Action of bromine and iodine on gelatin, VIII, 592
- COLE.** Glyoxylic acid in acetic acid, IX, 90  
Tryptophane, Adamkiewicz's reaction for, VII, 351  
test for, VII, 252
- COBURN and SPILLER.** Examination of sod oils, II, 509
- and **PINKUS.** Albumin, VIII, 91
- SAVORY.** Bence-Jones protein, VIII, 91
- HOPKINS, GOWLAND.** See *Fletcher*.
- HOPPENSTEDT.** Estimation of free acid in tan-liquors, V, 97  
Tests for tannins and hemlock, IX, 403
- HOPPE-SEYLER.** Hæmoglobin, estimation of, VIII, 561  
Hyaline cartilage, human, composition of, VIII, 624  
Keratoids, VIII, 673  
Phytosterol from maize and rape and almond oils, II, 485  
Yeast, fat content of, I, 209  
nitrogenous constituents of, I, 208
- HORBACZEWSKI, J.** Composition of urinary calculi, VII, 386
- HORLEIN.** See *Knorr*.
- HORN.** Grape seed oil, II, 175
- HORN, F. M.** Estimation of benzoic acid in milk, III, 413
- HORNE.** Use of anhydrous basic lead acetate in polarimeters, I, 310
- HORTON.** Hexamethylene-tetramine, detection of, in medicines, I, 263
- HORTON, EDWARD.** Aromatic acids, III, 391; IX, 279  
Berberine and its associates, VI, 551; IX, 521  
Naphthylamines and their allies, IX, 475  
See *Armstrong*.
- HORTVET.** Adulteration of cider vinegar, IX, 95  
of maple products, I, 389
- HORWITZ.** Presence of cholesterol in oils in dyeing fabrics, II, 511
- HOUDÉ.** Poisoning by columbin, VI, 577  
and **LABORDE.** Sparteine, VI, 232
- HOUGH.** Determination of the acidity of hide powder, V, 81
- HOUGHTON.** Ammonia, removal of, from mixtures with pyridine, IX, 476
- HOWARD.** Morphothebaine, VI, 406  
and **HODGKIN.** Homoquinine, VI, 549  
**STEPHENSON.** Crystalline form of the salts of opium alkaloids, VI, 439
- HOWARD, A. G.** Analysis of coca leaves, VI, 345
- HOWARD, B. F. and CHICK, O.** Cinchonamine nitrate, VI, 548  
**PERRY, F.** Salts of cinchonamine, VI, 547
- HOWARD, D.** Cinchona bark, alkaloids in, VI, 484  
estimation of quinine in, VI, 493  
Kerner test for quinine sulphate, VI, 521  
Quinine sulphate, detection of other alkaloids in, VI, 523
- HOWARD, H.** See *F. G. Pope*.
- HOWARD, W. C.** Amorphous cocaine, VI, 342
- HOWE, PAUL E.** Ninhydrin test for amino-groups, IX, 560
- HOYER.** See *Connstein*.
- HUBBARD.** Estimation of vanillin, IX, 307
- HUBER.** See *Kaufmann*.
- VON HUBER.** See *Schwars*.
- HUDSON and HARDING.** Estimation of raffinose, IX, 625  
**PAINE.** Preparation of invertase solution, IX, 46
- COX and SIMMONS.** Detection of adulteration of rose-oil, IV, 387  
Rose ottos, IV, 389
- HUDSON, C. S.** Solubility of nicotine in water, VI, 238
- HUE.** See *Eiber*.
- HÜBENER.** Phenolsulphonic acid, estimation of, III, 397  
Rubber, estimation of, IX, 321  
in ebonite, IV, 146  
sulphur in, IV, 126  
in vulcanised rubber, IV, 135
- HÜBENET.** Estimation of sulphur in vulcanised rubber, IV, 140

- HÜBL. Beeswax, estimation of cerotic acid in, II, 247, 248  
 Castor oil, solidifying point of the mixed fatty acids from, II, 161  
 Fats and oils, determination of the iodine value of, II, 29  
 Linseed oil, melting point of the fatty acids from, II, 350  
 Waxes, ratio number for, II, 253, 254
- HÜBLER. Preparation of colchicine, VII, 9
- HÜBSCHMANN. Acolyctine, VI, 275
- HÜFNER. Hæmoglobin, saturation of, with oxygen, VIII, 522  
 spectrum of, VIII, 521  
 and GANSSER, E. Molecular weight of oxy-hæmoglobin, VIII, 507
- KULZ. Spectrum of hæmoglobin, VIII, 521
- REINBOLD. Combination of methæmoglobin with nitric oxide, VIII, 540
- HÜHN. See *König*.
- HUERRE and LEMELAND. Analysis of tree gums, I, 440
- HÜTHIG. See *Walbaum*.
- HUGEL. See *Normann*.
- HUGGENBERG, W. See *E. Borshard*.
- HUGOUNENQ. Analyses of adulterated peptones, VIII, 397  
 and MOREL. Hydrolysis of proteins, VIII, 21
- HUGUENIN. See *Durand*.
- HUISCAMP. Fibrinogen, VIII, 91  
 Nucleoprotein of thymus, VIII, 92
- HUIZINGA, D. Extraction of glycogen, VIII, 376
- HULTON, H. F. E. See *Baker, J. L.*
- HUMBERT, M. Detection of horse flesh in sausages, VIII, 377
- HUMBOLT. Origin of bitumens, III, 37
- HUMMEL. Analysis of raw wool, VIII, 682
- HUMMEL, J. J. Examination of dyed fibres, v, 486
- HUMPHRIES and BIFFEN. Strength of wheat flour, I, 453
- HUNT, B. Estimation of tannins, v, 62, 67
- HUNZIKER. Methods of obtaining cream, VIII, 181  
 and SPITZER. Analyses of condensed milk, VIII, 210
- HURST. Gamboge, v, 417  
 Lubricating greases, determination of the water in, III, 179  
 Valenta test for fats and oils, II, 63
- HURTER. Estimation of ferrocyanides in sodalies, VII, 513
- HURTLEY. See *Clarke*.
- HUSEMANN. Phytosterol from *daucus carota*, II, 485
- HUSEMANN, T. Arsenical ptomaines, VII, 355
- HUSMANN. See *Koenigs*.
- HUTCHINSON, C. H. Influence of special conditions on the reducing power of sugar solutions, I, 336
- HUTH. See *Erdmann*.
- I
- IEL, A. Test for vanillin, III, 516
- INAGAKI. Albumin, VIII, 91
- INAGAKI. Serum-albumin, crystalline, preparation of, VIII, 67
- INCE. See *Dunstan*.
- INCE, W. H. Test for gallic acid with ferrous sulphate, III, 528
- INCHLEY. Specific gravity of defibrinated blood, VIII, 498
- INGHAM. Saffron, v, 419
- INGLE. Linoleum, II, 362  
 Linseed oil, drying of, IX, 199  
 effect of heat on, IX, 200  
 hexabromide test for, IX, 190  
 iodine value for, IX, 188
- ILJIN. Rotatory power of tannic acid, v, 17
- IMAI. See *Fesca*.
- IMBERT. Estimation of protocatechuic acid, III, 512  
 and PAGES. Estimation of glycerophosphates, II, 452
- IMPERIAL COMMISSION OF NORMAL STANDARDS. Table for the transformation of specific gravity into degrees Baumé (rational), I, II
- IONINE. See *Schützenberger*.
- IRK. Hungarian spearmint oil, IX, 372
- ISHIKAMA, I. Analysis of tannin-yielding materials, v, 32
- ISHIKAWA. Reduction equivalent of gallotannic acid, v, 64
- ISSOGLIO. See *Possello*.
- ITALIAN GOVERNMENT COMMISSION. Silver nitrate test for cottonseed oil, II, 136
- V. ITALLIE. Aloes, analysis of, VII, 148  
 Castor oil, solubility of, in absolute alcohol, II, 162  
 Lacmoid, use of, as an indicator in the estimation of alkaloids, VI, 182  
 Macassar oil, specific gravity of the mixed insoluble fatty acids from, II, 194  
 Venice turpentine, constants for, IV, 77  
 and KERBOSCH. Opium alkaloids, IX, 504
- IZRAILSKY. See *Krimberg*.
- J
- JAARVELD and STOKVIS. Hippuric acid, estimation of, VII, 395  
 Urine, benzoic acid in, IX, 574
- JABLIN-GONNET. Occurrence of salicylic acid in wild cherries, III, 466
- JACKSON. See *Dunstan*.  
 and COMEY. Action of fuming nitric acid on potassium cobalticyanide, VII, 533
- MENCKE. Preparation of curcumin, v, 414
- YOUNG. Fractional distillation of hydrocarbons, IX, 229
- JACKSON, R. Estimation of tannin, v, 88
- JACOBS. See *Levene*.
- JACOBSEN. Detection of geraniol, IV, 260
- JACOBSEN, O. Test for benzoic acid from gum benzoin, III, 408
- JACOBSON. See *Frank*.
- JACOBSON. Constitution of primuline, v, 371  
 Phytosterols from beans, peas and lupins, II, 486

- JACOBY. Measurement of protein hydrolysis, VIII, 11  
Salicylic aldehyde test for oxydases, VIII, 14
- JACQUE. Estimation of nitrogen in nitrocellulose, III, 565
- JACQUEMIN. Cyanogen; preparation of, VII, 454  
Nitrobenzene, detection of small quantities of, III, 213  
Phenol, detection of, III, 296
- JAECKLE. Roasting of coffee, VI, 648
- JAFFÉ. Detection of indoxyl-sulphuric acid in urine, VII, 255  
See *Richardson*.
- JAGERSCHMID. Test for caramel, V, 640
- JAGO. Strength of flour, I, 453; VIII, 100
- JAHNS. Agaric acid, IV, 5  
Areca palm, alkaloids from, VI, 208, 210, 211  
Thyme oil, IX, 377  
Worm-seed, isolation of choline and betaine from, VII, 279
- JAKOB. See *von der Heide*.
- JAMA, A. Roman chamomile oil, IV, 329
- JANOVSKY. Reactions of  $\alpha$ - and  $\beta$ -toluylene-diamine, VI, 107
- JANSENS and LEBLANC. Nucleus of yeast cell, I, 207  
See *Dangeard*.
- JAQUET. Salicylic aldehyde test for oxydases, VIII, 14
- JAUBERT. Hydroxyaposafranone, V, 322
- JAUNNES, L. Substitute for coffee beans, VI, 664
- JAVILLIER. Antipyrine, test for, IX, 470  
Croton oil, effect of method of extraction on the constants for, II, 172  
See *Bertrand*.
- JAVILLIER, O. Estimation of atropine, IX, 493
- JAWOROWSKI. Test for berberine, VI, 555
- JAY. See *Curtis*.
- JAYNE, H. W. Preparation of phenol, III, 289
- JEAN. Dégras, II, 504, 507, 508  
Lard and its substitutes, refractometer values for, II, 319  
Leather, estimation of free acid in, V, 109  
Nutmeg butter, composition of, II, 182  
Sunflower oil, unsaponifiable matter in, II, 154  
See *Amagat*.  
and FRABOT. Detection of foreign colouring matters in wines, I, 180  
REMONT. Separation of resin and fatty acids, IV, 33
- JEAN, F. Arachis oil, estimation of, II, 99  
Colophony, acid resins in, IV, 23  
Egg-yolk, composition of, VIII, 436  
Tannins, estimation of, V, 92
- JEANCARD and SATIE. Hyssop oil, IV, 345  
Neroli oil, IV, 367  
Rose oil, IV, 389
- JEDLIKA. Detection of pseudotannins, IX, 409  
Oak extract, V, 82; IX, 397
- JEFFERS. See *Thorne*.
- JELLINEK. Detection of impurities in commercial flavopurpurin, V, 214
- JENKINS. Borates, detection of, in milk, VIII, 174  
Fats and oils, bromine thermal process for, II, 61  
gravimetric determination of the bromine value for, II, 28  
Lard oil, acidity of, II, 197  
constants of, II, 198  
specific gravity of, II, 198  
Tung oil, II, 155, 156, 157
- JENKS. See *Cross*.  
and BEDFORD. Estimation of higher alcohols in potable spirits, I, 195
- JENSEN. Aniseed oil, IX, 351  
Cinnamoin, iodine value of, IX, 296  
Coconut oil, composition of, II, 188  
Linseed oil, hexabromide test for, IX, 190  
Morphine, estimation of, IX, 505  
and PLATTNER. Formation of a skin on milk, VIII, 125
- JENSEN, J. P. H. See *O. Winge*.
- JERUSALEM. Estimation of lactic acid, VII, 439  
See *von Farkh*.
- JESSEN-HANSEN. See *Sørensen*.
- JOACHIM. See *Freund*.
- JOASTART, N. See *L. L. Dekoninck*.
- JOBST. Analyses of commercial quinine tannate, VI, 530
- JØRGENSEN. Borates, estimation of, in milk, VIII, 174  
Morphine, extraction of, from animal organs, VI, 438  
Saccharin, detection of, in foods and beverages, III, 432  
Yeast, cell wall of, I, 206  
culture, I, 216, 217, 219  
tannin in, I, 209
- JOFFRE. Examination of dyed fibre, V, 486
- DE JOGG, K. Assay of coca leaves, VI, 346
- JOHANN. See *Oosterla*.
- JOHANNIS. Calcium cyanide, decomposition of, VII, 475  
Hydrated barium cyanide, preparation of, VII, 476  
Sodium cyanide, preparation of, VII, 472
- JOHANSEN. Estimation of tannins, V, 85
- JOHNS, C. O. Isomers of theobromine and caffeine, IX, 525
- JOHNSON. Enzymes, determination of the diastatic power of, VIII, 5  
mastic, melting point of, IV, 59  
See *Harries, Walker*.
- JOHNSON, A. E. Analysis of coffee mixtures, VI, 662  
Weight of copper and copper oxide obtained from the principal sugars, I, 569
- JOHNSTONE, W. Commercial pepper, VII, 57  
Production of piperidine by the distillation of pepper, VI, 141
- JOLLES. Acetone, estimation of, I, 107  
Pentoses, estimation of, in urine, I, 400  
Pyramidone, detection of, in urine, VI, 49  
Sugars, estimation of, IX, 56
- JOLLES, A. Estimation of hæmoglobin, VIII, 561
- JONES. Ipecacuanha alkaloids, estimation of, VII, 43



- JONES. Valenta test for fats and oils, II, 63  
 See *Engelhardt, Gamgee.*  
 and WHIPPLE. Nucleoprotein of suprarenals, VIII, 92  
 WOOTTON. Separation of hydrocarbons, IX, 232
- JONES, BREESE. See *Osborne.*
- JONES, G. C. Alcohols, I, 85; IX, 1  
 Wines and spirits, I, 165; IX, 13  
 Malt and brewing materials, IX, 5  
 Non-glucosidal bitter principles, VII, 137; IX, 549  
 See *A. R. Ling.*
- JONES, J. R. See *A. G. Green.*
- JONESCU, ANNA. Detection of benzoic acid in food, III, 411
- DE JONG. Estimation of cinnamic acid, III, 438; IX, 292
- JORISSEN. Clove oil, composition of, IV, 330  
 Hydrastinine hydrochloride, reaction of, VI, 573  
 $\alpha$ - and  $\beta$ -Naphthol, distinction between, III, 254  
 and GROSJEAN. Formation of solanidine from solanine, VII, 92
- JORISSEN, A. Detection of cinnamic acid in commercial benzoic acid, III, 407
- JORISSEN, W. P. and RUTTEN, J. Estimation of naphthalene by the picrate method, IX, 236
- JOUILLARD. Estimation of the fatty acids in turkey-red oil, II, 170
- JOWETT. Atisine, VI, 278  
 Jaborandi, alkaloids of, VII, 51, 53  
 Pilocarpine and its salts, VII, 51  
 Pilocarpus microphyllus alkaloids, IX, 537  
 Tropeines, artificial, VI, 301  
 See *Dunstan.*  
 and POTTER. Salinigrin, VII, 100  
 PYMAN. Mydriatic properties of tropeines, VI, 301
- JUCKENACK. Detection of colouring matters in food, V, 652  
 See *Hilger.*  
 and PASTERNAK. Mean molecular weights of soluble and insoluble fatty acids from butter fat, II, 287  
 Melting point of cholesteryl acetate of butter, II, 301
- JÜRGENS, A. Comparison of Schreiner's spermine with that of Pöhl, VII, 203
- JUILLARD, P. Action of sulphuric acid on oleic acid, II, 410
- JULIUS. Estimation of aniline, VI, 59
- JUMEAU. Presence of ammonium thiocyanate in commercial ammonium sulphate, VII, 545
- JUNGFLEISH and GODCHOT. Dilactylic acid, VII, 446
- JUNGFLEISCH, E. Kerner test for quinine sulphate, VI, 521
- JUNK. See *Bergmann.*
- JURGENS. Composition of aconitine, VI, 258
- JURRISEN. See *Berl.*

## K

- KACHLER. Caprinic acid, IV, 329  
 Essential oils, colouring matter in, IV, 252
- KACHLER, G. Melting points of mixtures of cinnamic and benzoic acids, III, 436
- KAHAN. Benin copal, IX, 310
- KAHN and ROSENBLOOM. Urinary calculi, analyses of, IX, 580
- KAILAN. Specific gravity of anhydrous glycerol, IX, 211
- KAJURA. See *Rosenheim.*
- KALLE and Co. Glycerol lactates, VII, 448
- KALMANN. Estimation of free organic acid in glue, VIII, 611
- KAMETAKA. Bloemargaric acid, II, 155  
 Japanese wood oil, IX, 144
- KAMMERER. See *Bensinger.*
- KANAI. See *Yoshimura.*
- KANE. Preparation of azolitnin, V, 429
- KANOLDT. Saffron, V, 420.
- KANTHACK and CADDY. Use of de-emetised ipecacuanha, VII, 49
- KAPELLER and GOTTFRIED. Bouillon cubes, IX, 617
- KARAS. Estimation of saccharin, IX, 291
- KARA-STOJANOW, CHARALAMPI. Alkaloids of stavesacre, VII, 15
- KARCZAG. See *Neuberg.*
- KARSCH. See *König.*
- KASSLER. Candle nut oil, II, 149
- KASSNER, G. Cattle poisoning from potato-residues, VII, 93  
 Ferricyanides, estimation of, VII, 529  
 Potassium ferricyanide, manufacture of, VII, 524
- KART. Supercooling of nitroglycerin, III, 570  
 and LAGAI. Sulphur in petroleum, III, 40
- KASTLE. Guaiacum test for blood, VIII, 523  
 Oxydases, VIII, 12  
 Phenolphthalin test for blood, VIII, 525  
 for oxydases, VIII, 13  
 Saccharin, test for, III, 431
- KATZ. Caffeine, estimation of, in tea, VI, 609  
 extraction of, from coffee, VI, 650  
 Flesh, mineral constituents of, VIII, 293  
 Santonin, estimation of, in santonica, VII, 155
- KATZ, J. Titration of cinchona alkaloids, VI, 497
- KAUDER, E. Modification of Hesse's method for the separation of opium bases, VI, 372  
 Sulphuric acid test for opium bases, VI, 367
- KAUFFMANN, HUGO. Effect of auxochromic groups, V, 237
- KAUFLER, F. See *R. Gnchm.*
- KAUFMANN and HUBER. Constitution of cinchona alkaloids, IX, 515
- KAY and APPLEBYARD. Estimation of picric acid, III, 580  
 BASTOW. Percentage of tannin in tannin yielding materials, V, 32
- KAY, P. Estimation of picric acid, III, 579
- KAYE. See *Schidrowitz.*
- KAYSER. Culture yeast, I, 215, 218  
 Essential oil from saffron, V, 418



- KEANE.** Formulæ for obtaining specific gravity by means of Baumé's hydrometer, I, 8
- KEBLER.** Beeswax, estimation of hydrocarbons in, II, 260  
Black walnut oil, constants for, II, 158  
Opium, assay of, VI, 428  
Spermaceti, commercial, II, 275  
See *Pancoast*.
- KEBLER, L. B.** Gurjun balsam, IV, 88  
Acetanilide, estimation of, in vanillin, III, 515  
Cineol, estimation of, in eucalyptus oils, IV, 340  
Copaiba, commercial, IV, 87  
Guaiacol, estimation of, in creosote, III, 356  
and H. C. FULLER. Pure glycerin, IX, 220
- KEEBLE and ARMSTRONG.** Benzidine as an oxydase reagent, IX, 591  
Identification of oxydases in plants, VIII, 13
- KEHRMANN.** Formulæ of azines, oxazines, and thiazines, V, 318  
Formula for hydroxyfluorones, V, 290  
and MESSINGER. Eurydols, V, 321  
Synthesis of rosinduline, V, 340
- KEHRMANN, F.** Constitution of oxazines, V, 341  
and WENTZEL, F. Triphenylcarbinol and its salts, V, 238
- KEISTEN.** See *Siegfeld*.
- KEITH.** See *Forbes*.
- KEKULÉ.** Phenol sulphonic acids, III, 393
- KELHOFER.** Detection of excess of alkali in cresylic acid sheep dips, III, 331
- KELLAS.** Melting point of *m*-hydroxybenzoic acid, III, 466
- KELLE.** Production of guaiacol from 1-2 anisidine, III, 343
- KELLER.** Alkaloids, estimation of, VI, 179  
percentage of, in ipecacuanha, VII, 48  
Caffeine, estimation of, in tea, VI, 609  
Ergot alkaloids, detection of, VII, 20  
estimation of, VII, 21
- KELLER, C. C.** Ipecacuanha, assay of, VII, 45  
Nicotine, estimation of, VI, 240  
Nux vomica, estimation of the alkaloids in, VI, 469, 472
- KELLER, O.** Bitter constituents of lupine seeds, VI, 229
- KELLING.** Presence of thiocyanates in the intestines, VII, 543
- KELLNER, O.** Tea, estimation of tannin in, V, 67  
of total proteins in, VI, 628  
Tea-plant, analysis of the leaves of, during six months, VI, 598
- KELLY.** See *Frankel*.
- KEMMERICH, E.** South American meat-extract, VIII, 397
- KEMP.** Preparation of cyanogen, VII, 454
- KEMPF.** Inks, writing, estimation of tannin in, IX, 468
- KENDALL.** See *Sherman*.
- KENRICK, E. B.** Analyses of tea after infusion, VI, 624
- KERBOSCH.** Alkaloids, formation of, in opium-poppy, IX, 477  
See *Van Itallie*.
- VAN KERCKHOFF.** Keratoids, VIII, 673
- KERN.** See *Fassbender*.
- KERNER.** Test for cinchonidine in quinine sulphate, VI, 520
- KERR.** Chestnut extract, manufacture of, V, 38  
Nickel in hydrogenated cottonseed oil, IX, 125
- KERR, G. A.** Detection of mangrove in quebracho, IX, 398, 399
- KERSTEIN.** See *Schmidt*.
- KESAVA-MENON.** Reichert-Meissl value for ghee, IX, 175
- KESSLER.** See *Hinsberg*.
- KETO, E.** Composition of copaiba balsam, IV, 82
- KETTLE.** See *Cocking*.
- KHARICHKOV, K. U.** Creosote, antiseptic properties of, IX, 276
- KICKTON, A., and KOENIG, W.** Detection of colour in sausages, V, 650
- KIEFFER, L.** Assay of opium, VI, 429  
Estimation of morphine, VI, 384
- KIELMAYER.** Lactolin, VII, 447
- KIENER.** See *Engel*.
- KILIANI.**  $\alpha$ - and  $\beta$ -Antiarin, VII, 124  
Digitonin, compounds of, with alcohols, VII, 118  
Digitoxin and gitalin, separation of, IX, 547  
Lactic acid, formation of, from carbohydrates, VII, 430  
Mucic acid, percentage of, from gums, I, 441
- KING.** See *Orton*.
- KING, P. E.** See *A. G. Green*.
- KINGZETT, C.** Composition of cacao butter, II, 177
- KINGZETT, C. T.** Rotation of turpentine oil, IV, 406  
Russian turpentine oil, IV, 402
- KIPPENBERGER.** Alkaloids, behaviour of, with indicators, III, 556; VI, 182  
estimation of, by means of iodine, VI, 190  
salts of, VI, 185  
use of Mayer's reagent in the estimation of, VI, 196  
vegetable, isolation of, VI, 178  
Antipyrine, estimation of, VI, 43  
Cinchona alkaloids, titration of, VI, 497  
Nicotine, detection of, by the formation of Roussin's crystals, VI, 238  
estimation of, VI, 241  
Sparteine, use of phenolphthalein in the estimation of, VI, 181
- KIPPING.** Sulphonation of camphor, IV, 203
- KIRCHER.** See *Schmidt*.
- KIRCHHOF.** Estimation of india-rubber, IX, 321
- KISCH.** See *König*.
- KISSLING.** Ash of bone glue, VIII, 610  
Glue, estimation of the non-gelatinous substances in, VIII, 612  
test for, VIII, 606  
Nicotine, estimation of, VI, 240, 250  
Tobacco, estimation of non-volatile acids in, VI, 249  
smoke, VI, 252
- KISSLING, RICH.** Determination of the solidifying point of paraffin scale, III, 195
- KISTIAKOFFSKY.** Preparation of glycogen, VIII, 376

- KITA. Action of taka-diastrase on starch, IX, 72
- KITT. Colophony, carboxyl value of, IV, 28  
Egg oil, II, 203, 204  
analysis of, VIII, 435  
Linseed oil, boiled, II, 354
- KJELDAHL. Inversion by yeast in the presence of thymol, I, 315, 343  
Measurement of diastatic activity of malt, I, 136
- KJELDAHL, J. Choline in beer, VII, 276
- KLAPROTH. Estimation of lactic anhydride in commercial lactic acid, VII, 442
- KLARFELD, H. See *R. Zoologicki*.
- KLASON. Estimation of thiocyanates, VII, 552  
Test for thiocyanates, VII, 548  
and NORLIN. Specific gravity of ethyl alcohol, I, 110  
of methyl alcohol, I, 86
- KLAVERNESS. See *Tschirck*.
- KLEBER. Estimation of citral, IX, 338  
See *Power, Stolman*.
- KLEE. Alkaloids, function of, in plants, IX, 478  
Thebaine and iso-thebaine, IX, 502
- KLEIN. Curcas oil, composition of, II, 174  
constants for, II, 175  
Olive-kernel-oil and bagasses-oil, II, 119
- KLEIN, C. A. Linseed oil, II, 323; IX, 180  
See *Davis*.
- KLEIN, O. Detection of colour in sausages, V, 650  
Portuguese oils, IX, 133
- KLEINSCHMITT. Hydrolysis of hordein, VIII, 104
- KLEINSTÜCK. Specific gravity of Japan wax, II, 192
- KLEY, P. Detection of exhausted leaves in tea, VI, 632
- KLIMONT. Borneo tallow, II, 176  
as a substitute for cacao butter, II, 179  
Cacao butter, composition of, II, 177  
Chinese vegetable tallow, composition of, II, 181  
Linseed oil, refraction constants of, IX, 192
- KLING. Estimation of tartaric acid, IX, 105  
and FLORENTIN. Estimation of tartaric acid, IX, 105
- GELIN. Estimation of tartaric acid, IX, 106
- GOBERT. Estimation of tartaric acid in fruit juices, IX, 107
- KLINGER and BUJARD. Detection of cochineal carmine in sausages, VIII, 380
- KLOBB. Arnidiol, II, 488  
Anthesterol, II, 488
- KLOSTERMANN. Digitonin test for butter, IX, 164
- KLUNGE. Test for aloes, VII, 144
- KLUYVER. Analyses of commercial glucose syrups, IX, 11  
Pentoses in plant extracts, IX, 63
- KNAPP. Dextrose, estimation of, I, 337  
Nickel in hardened oils, IX, 125
- KNAPP, A. W. See *H. S. Shrewsbury*.
- KNEBEL, E. Kolanin in kola-nuts, VI, 682
- KNECHT. Dyeing of wool and silk, VIII, 687  
Indigotin, estimation of, V, 400, 403  
Lanuginic acid, VIII, 685  
See *Benedikt*.  
and HIBBERT. Estimation of hæmoglobin, VIII, 561
- KNECHT and RAWSON. Examination of dyed fibres, V, 486
- KNECHT, E. Determination of dyestuffs, V, 479  
Test for paranitraniline red in fibres, V, 488
- KNITL. See *Tschirck*.
- KNORR. Extraction of meat bases, VIII, 303  
See *Ach*.  
and HORLEIN. Constitution of morphine, VI, 356
- KNOWLES. Tannin in dyeing processes, IX, 405
- KNOX and PRESCOTT. Composition of kola seeds, VI, 681  
of kolanin, VI, 682
- KNUBLAUCH. Estimation of cyanogen in spent gas purifying mass, VII, 516
- KNUBLAUCH, O. Estimation of ferrocyanides, VII, 512
- KOBER. Enzymes, IX, 591
- KOBERT. Antidote for cyanide poisoning, VII, 470
- KOBERT, R. Orthine, VI, 32
- KOCH. See *Thatcher, Treadwell*.
- KOCHS. Mucilage in linseed husks, II, 327
- KODAMA. Caviare, IX, 622
- KÖCHLIN, H. Gallocyanine, V, 344
- KÖCHLIN. Tannates as colour bases, V, 118
- KÖNIG. Coffee adulterants, composition of, VI, 675  
berries, addition of glucose-syrup to, VI, 670  
composition of, VI, 644  
roasting of, VI, 649  
substitute, VI, 664  
Crude fibre, estimation of cellulose, lignin and cretin in, I, 437  
European honeys, composition of, I, 383  
Fish-roe and caviare, composition of, VIII, 460  
Flesh, amount of creatine in, VIII, 287  
composition of the ash from, VIII, 292  
of wild animals and birds, analyses of the, VIII, 263  
Maté, analyses of, VI, 641  
Meat, canned, analysis of, VIII, 336  
cold-water extract of, VIII, 298, 300  
composition of, VIII, 262  
estimation of moisture in, VIII, 296  
Muscle, pure, composition of, VIII, 278  
Nicotine, estimation of, IX, 485  
Peptones, valuation of, VIII, 396  
Phytosterol from meadow hay, II, 485  
Potable spirits, analyses of, I, 199  
Sausages, analyses of, VIII, 358  
Tea, analyses of various kinds of, VI, 599  
Van Houten's cocoa, analysis of, VI, 692  
Wheaten bread, analyses of, I, 459  
Xanthine bases, estimation of, in meat extracts, VIII, 413  
See *Greifenhagen*.  
and BÖMER. Composition of meat extracts, VIII, 397, 421  
GROSZELD. Caviare, IX, 622  
HÖRMANN. Dextrin-like substance in coniferous honey, I, 388  
HÜHN. Estimation of cellulose, IX, 77  
KARSCH. Differentiation between pure and adulterated honey, I, 388

- KONIG and KIRSCH. Estimation of albumose and peptone, VIII, 396
- KOENIG. Extraction of indigo, IX, 429  
See *Bullenberg*.
- KOENIG, W. See *A. Kichlon*.
- KOENIGS and HUSMANN. Conversion of cinchonine to cinchonidine, VI, 538
- KÖNIGS. Limitation of the term vegetable alkaloids, VI, 167
- KÖNIGS, E. Analysis of weighted silk, VIII, 657
- KOERNER. See *Fischer*.
- KOESTLER. Cheese, fat of, VIII, 246  
Emmentaler cheese, analysis of, VIII, 251  
Margarine cheese, analyses of, VIII, 254
- KÖTTSTORFER. Saponification value for butter fat, II, 286
- KOETTSTORFER. Estimation of the saponification value of oils, II, 15  
Examination of fats, I, 232
- KOHLER. Tests of asphalt lutes and cement, III, 98
- KOHLER, O. Herabol myrrh, IV, 98
- KOHN and FRYER. Colour change in moist phenol, III, 293
- KOHN, C. A.  $\alpha$ -Hydroxyhydroethylene-quinoline, VI, 503
- KOHNSTEIN. Tannin material in leather, IX, 414  
and SIMAND. Estimation of volatile organic acids in tan-liquors, V, 98
- KOLB. Hydrometer of, I, 9
- KOLBE and LAUTEMANN. Preparation of salicylic acid, III, 467
- KOLBE, H. Test for the purity of salicylic acid, III, 470
- KOLLO. Tests for halogen salts in pyramidone, VI, 49
- KOLLO, I. Assay of bismuth salicylate, III, 491
- KOMMPA. Synthesis of camphor, IV, 202
- KONDAKOW and SCHINDELMEISER. Synthesis of  $\beta$ -phellandrene, IV, 171
- KONDO. Chondroitin-sulphuric acid, IX, 575
- DEKONINGH. Estimation of ferrocyanides in spent gas purifying mass, VII, 516  
See *Muter*.
- DE KONINGH, L. Estimation of mineral matter in rubber, IV, 120  
of solids in beef tea, VIII, 397
- KONOWALOFF. Action of nitric acid on paraffins, III, 2  
Mono-nitro-compounds of polymethylenes, IX, 237
- KONSTEIN. Test for tannins, IX, 403
- KOPECKY. Estimation of tannins, V, 95
- KOPP. Specific gravity of benzene, III, 203
- KOPPE. See *Tiemann*.
- KOPPESCHAAR. Indirubin, extraction of, V, 397  
Phenol, estimation of, III, 300  
Quinine sulphate, VI, 515  
optical assay of, VI, 525
- KORENTSCHEWSKI and ZIMMERMANN. Properties of soja-bean oil, II, 146
- KORMANN. See *Sachsse*.
- KORNAUTH, C. Composition of the ash of coffee, VI, 654
- KORNECK. Estimation of india-rubber, IX, 321
- KORSAK. See *Thann*.
- KOSSANOWSKI, J. Preparation of santonin, VII, 152
- KOSSEL. Agmatine guanidylbutylamine, formation of, from herring spawn, VII, 351  
Amino-acids formed by the hydrolysis of salmine, VIII, 20  
Histone, VIII, 92  
Protamines, VIII, 92  
Proteins, extraction of, VIII, 48  
Theophylline, VI, 595  
Xanthine, isolation of, VI, 580  
Yeast, nitrogenous constituents of, I, 208  
and DAKIN. Amino-acids formed by the hydrolysis of salmine, VIII, 20  
KUTSCHER. Amino-acids formed by the hydrolysis of gelatin, VIII, 20  
Diamino-acids formed by protein hydrolysis, separation of, VIII, 28  
Gadus histone, VIII, 91  
Histone, VIII, 92  
Spongin, hydrolysis of, VIII, 672  
and PATTEN. Separation of diamino acids formed by protein hydrolysis, VIII, 28  
and OBERMÜLLER, K. Isolation of cholesterol, II, 490
- KOSTANECKI. Constitution of tannin, V, 19  
and TAMBOR. Catechins from gambier, V, 30
- KOTTMAYER. Percentage of alkaloids in ipecacuanha, VII, 48
- KOZAI, Y. Analyses of tea, VI, 600  
Facing in green tea, VI, 630
- KRÄMER. Estimation of acetone, I, 107
- KRAEMER and SINDALL. Pepper, adulteration of, VII, 58  
analysis of, VII, 64  
and SPILKER. Hydrocarbons, aromatic, estimation of, IX, 263
- KRAFFT.  $\alpha$ -Monopalmitin, II, 397
- KRAFT. Digitoxin and gitalin, separation of, IX, 547  
Hydro-ergotinine, VII, 16
- KRAMER. Pure yeast culture in cider manufacture, I, 218
- KRAMERS. See *Pictet*.
- KRAPPS and STERN. Hydrolysis of soap, II, 417
- KRASSER. Bouillon cubes, IX, 618
- KRAUSE. Viscosity of mineral oils, III, 147
- KRAUT. Estimation of cuminol in cumin oil, IV, 334
- KRAUTH, C. Analyses of coffee and its adulterants, VI, 675
- KRAWKOW. Amyloid, VIII, 91
- KREIDL and NEUMANN. Microscopical examination of calcium casein, VIII, 118
- KREIS. Furfural-aldehyde test for rancid sesame oil, II, 144  
Phloroglucinol test for almond-kernel and peach-kernel oils, II, 104  
Sesame oil, II, 142  
and HAFNER. Lard and beef fat, crystals from, II, 318, 321  
fatty acids from, II, 389  
Palmitic acid, solubility of, in alcohol, II, 396

- KREIS and HAFNER. Stearic acid, estimation of, II, 394, 395  
and ROTH. Colour test for hardened marine animal oils, IX, 124
- KREIS, H. Detection of thiophen in benzene, III, 210
- KREMEL. Constants for myrrh and bdellium, IV, 101
- KREMEL, A. Amber, analysis of, IV, 20  
Ammoniacum, IV, 92  
Colophony, acid values of, IV, 26  
Galbanum, constants for, IV, 97  
Guaiacum, IV, 66  
Gum-resin from asafetida, IV, 95  
Mastic, IV, 60  
Resins, constants for, IV, 10, 12, 13  
Sandarac, IV, 58  
Storax, crude, analysis of, III, 463  
Venice turpentine, constants for, IV, 77
- KREMERS. Dark colour of oil of wild bergamot, IV, 252  
and SCHREINER. Estimation of phenols in thyme oil, IV, 399
- KREMERS, E. Commercial turpentine oil, IV, 404  
Estimation of carvone, IV, 214
- KRETSCHY. See *Barth*.
- KRIES. Detection of rancidity in meat fat, VIII, 319
- KRIMBERG and IZRAILSKY. Creatinine from meat extracts, IX, 615
- KRÖBER. Estimation of pentoses and pentosans with phloroglucinol, I, 401, 403
- KROEBER. See *Lindner*.
- KROGH. Saturation of hæmoglobin with oxygen, VIII, 522
- KROPP and DECKER. Formula for hydroxy-fluorones, V, 290
- KRÜGER. Adenine, VI, 596  
Benzoic acid, estimation of, in meat, IX, 285  
in sausage, IX, 619
- KRÜGER, M. Precipitation of xanthinoid substances containing a substituted NH-group by cupric sulphate, VII, 324
- KRUG. Estimation of caffetannic acid in coffee, VI, 658  
See *MacElroy*.
- KRUGEL. See *Ladenburg*.
- KRUGER. See *Tiemann*.
- KRUGER, J. See *G. Grube*.
- KRUKENBERG. Cornein, VIII, 91
- KRUKENBERG, C. F. W. Action of hydrochloric acid on chitin, VIII, 671
- KRUMBHAAR. Estimation of absorption of oxygen during drying of oils, IX, 121  
Oxygen absorption of linseed oil, IX, 193
- KRUSS and MORAHT. Compound formed by the addition of potassium thiocyanate to a ferric salt, VII, 550
- KRUYSSSE, P. J. Separation of quinine from other alkaloids, IX, 516
- KRZIZAN. Presence of copper in food gelatin, VIII, 616
- KUBELKA. Estimation of tannin, IX, 404
- KÜGLER, K. Matico camphor, IV, 210
- KÜHL. Test for lactic acid, VII, 436
- KÜHN. See *Luerssen*.
- KÜHNE. Digestion of proteins, VIII, 472  
and CHITTENDEN. Estimation of albumose and peptone, VIII, 396  
Keratoids, VIII, 673, 675
- KÜHNE, W. Albumoses and peptones, VIII, 397
- KÜNG. See *Winterstein*.
- KÜNKLER. Flash point of linseed oil, II, 331
- KÖNTZE. Bacteriology of kephyr, VIII, 227
- KÜSPERT. See *Hofmann*.
- KÜSTER. Hæmatin and hæmatoporphyrin, oxidation products of, VIII, 557  
Hæmin, preparation of, VIII, 547  
Hæmopyrrole, VIII, 559  
Naphthalene estimation of, in the commercial product, III, 250  
 $\beta$ -Naphthol, estimation of, III, 258, 259
- KÜSTER, F. W. Estimation of solid hydrocarbons by their reaction with picric acid, III, 276
- KUFFERATH. See *Binz*.
- KUHLMANN. Formation of hydrocyanic acid from alcohol and nitrogen oxide, VII, 463
- KULZ. See *Hafner*.
- KUMAGAWA and SUTO. Extraction of fat from animal tissue, IX, 223
- KUNTZE. Bacillus of fermented milk, VIII, 224  
Test for mustard oil for pharmaceutical purposes, VII, 110
- KUNZ. Estimation of lactic acid, VII, 438
- KUNZ, H. Chrysotropic acid in belladonna root, VI, 311
- KUNZE, W. E. Estimation of theobromine and caffeine in cocoa, VI, 709
- KUNZ-KRAUSE. Emetine, constitution of, VII, 39  
Cyanogen, detection of, in coal gas, VII, 456  
Pyridine, detection of, IX, 475
- KURAJEFF. Plasteins, VIII, 495
- KURBATOW. See *Beilstein*.
- KUSSEROW. Determination of the fermenting power of yeast, I, 223
- KUTSCHEN. See *Kossel*.
- KUTSCHER. Estimation of bases in meat extracts, VIII, 414  
See *Ackermann, Engeland, Kossel*.

## L

- LA TOUR and NALPASSE. Opium, estimation of morphine in, IX, 504
- LA WALL, C. H. Japan wax, adulteration of, with starchy matter, II, 194  
Morphine, estimation of, IX, 505  
Spices, detection of colouring matters in, V, 659  
Thalleioquin test for quinine, IX, 516  
Vanillin, influence of, on tests for formaldehyde, I, 260  
and BRADSHAW. Estimation of benzoic acid in catsup, III, 413
- FORMAN. Detection of chicory in coffee extracts, IX, 532
- VAN DER LAAN and TIJDENS. Estimation of benzoic acid, IX, 284

- LABAT.** Atropine and hyoscyamine, test for, IX, 491  
Hydrastine, test for, VI, 567  
Narcotine, test for, VI, 402; IX, 501
- LABAT, A.** Estimation of pyridine, VI, 138
- LABAUNE.** See *Dupont*.
- LABBÉ.** Formation of isopulegol from citronellal, IV, 269  
and **MAGUIRO.** Estimation of albumin in eggs, IX, 621
- LABBÉ, H.** Absence of pinene in thyme oil, IV, 398  
Separation of carvone and limonene, IV, 216
- LABORDE.** Effect of cinchonine on the physiological effects of quinine salts, VI, 525  
Estimation of glycerol in wines, I, 167  
See *Houdé*.
- LACH, B.** Ozokerite from Colorado, III, 55  
crude, assay of, III, 56
- LACHMANN.** Hydrastine, VI, 564
- LACHOWICZ.** Galician petroleum, III, 43  
Preparation of benzoic anhydride, III, 417
- LADD.** See *Holley*.
- LADENBURG.** Coniine, synthesis of, VI, 211  
Hops, alkaloids in, VII, 173  
Piperidine, formation of, from cadaverine, VII, 348  
Pseudotropine, VI, 294  
Pyridine, purification of, VI, 132  
Tropeines, artificial, VI, 301  
separation of the, VI, 304  
See *Hofmann*.  
and **ABEL.** Composition of spermine, VII, 203  
**KRUGEL.** Melting point of acetone, I, 105  
methyl alcohol, I, 86  
Solidification of ethyl alcohol, I, 110
- VAN LAER.** Keratoids, VIII, 673  
Measurement of the catalytic action of malt, VIII, 15
- LAGAI.** See *Kast*.
- LAGERHEIM.** Ergot in flour, VII, 24
- LAGORCE, E.** Detection of cochineal, V, 423
- LAHRMANN.** See *Sudendorf*.
- LAIDLAW.** Cytisine, poisoning by, VII, 14  
Hæmatoporphyrin, preparation of, VIII, 552  
Indolethylamine, physiological properties of, VII, 351  
Pilosine, anhydro-pilosine and pilosinine, physiological action of, IX, 540  
See *Dale, Ewins*.
- LAIDLAW, P. P.** Turacin, VIII, 559
- LAJOUX.** Adulteration of glycerin with magnesium sulphate and glucose, II, 475  
See *Grandval*.
- LALLEMENT AVÉ.** Determination of the mean molecular weights of fatty acids from butter, II, 288, 289, 297  
Saponification value for German butters, II, 287
- LAMB.** Detection of sumac, IX, 399  
Determination of colour in tannin extracts, V, 96  
See *Gill*.
- LAMB, M. C.** Analyses of tanned hides, IX, 414
- LAMBERT.** See *Foster*.
- LAMPART and MÜLLER.** Strophantin, determination of, IX, 547
- LANDAUER, P. and WEIL, H.** Leuco-compound of methylene blue, V, 355
- LANDOLT.** Asparagine, optical activity of, VII, 236  
Camphor, specific rotation of, IV, 194  
Beet sugar, ratio between the potassium carbonate and the amount of organic salt in, I, 350  
Nicotine, specific rotation of, VI, 237  
Phenol, estimation of, III, 300  
Polarimetry, I, 46  
use of Aron's mercury vapour lamp in, I, 43  
and **BÖRNSTEIN.** Specific gravity, melting point and boiling point of chloroform, I, 274
- LANDSBERGER.** Shukoff and Schestakoff's method for the estimation of glycerol, I, 463
- LANDSTEINER and UHLIRZ.** Adsorption of proteins by colloids, VIII, 57  
Precipitation of proteins with colloids, VIII, 37
- LANE.** Estimation of castor oil in mixtures, II, 165, 167  
Iodine value of the liquid fatty acids from lard, II, 319  
See *Ling*.
- LANE, HEINZ C.** Test for mechanical pulp, IX, 87
- LANE, N. J.** Free fatty acid in olive oil, II, 109
- LANG.** See *Grandmougin*.
- LANGBEIN.** Estimation of *p*-sulphaminobenzoic acid in saccharin, III, 430  
See *Stohmann*.
- LANGDON, N. J.** Silk-weighting, VIII, 653
- LANGE.** Separation of  $\alpha$ -picoline from bone oil, VI, 143
- LANGE, WILLIAM.** Detection of sulphites in food gelatin, VIII, 617
- LANGIER.** Reconstruction of the original salts from the ash of cane and beet sugar, I, 350
- LANGLEY and DICKINSON.** Identity of nicotine and piturine, VI, 229
- LANGLOIS.** Formation of ammonium cyanide, VII, 472  
See *Genovesse, Portes*.
- LANGMUIR and WHITE.** Analysis of shellac, IX, 312
- LANGMUIR, A. C.** Iodine value of shellac, IV, 70
- LANGRIN.** See *Moissan*.
- LANGSTEIN.** Conalbumin, VIII, 91  
Globulins, VIII, 91  
*p*-Hydroxyphenylethylamine, formation of, in the prolonged peptic digestion of egg-albumin, VII, 346
- LANGWORTHY.** Composition of eggs, VIII, 440
- LANKESTER, E. RAY.** Occurrence of hæmoglobin, VIII, 506
- LAQUEUR and SACKUR.** Casein from cow's milk, basicity of, VIII, 124  
drying of, VIII, 118  
Caseinogen, titration of, VIII, 88
- LASCHE.** Detection of caramel in spirits, V, 656

- LASSAR-COHN. Estimation of bile acids, VII, 415
- LATSCHINOW. See *Engelhard*.
- LAUBER and STOREK. Use of thiocyanates as a mordant for alizarin-red, VII, 547
- LAUDER. See *Dobbie*.
- and TINKLER. Constitution of cotarnine, VI, 358
- WALDEN. Detection of traces of hydrogen cyanide, VII, 480
- Picrate reaction for hydrocyanic acid, VII, 470
- LAUTEMANN. Tetraiododiphenylenequinone, III, 483
- LAURAIN. Estimation of naphthalene in coal gas, IX, 268
- LAURENT. Polarimeter, I, 42
- Yeast glycogen, I, 209
- LAUROW. Plasteins, VIII, 495
- LAUTEMANN. See *Kolbe*.
- LAUTH and GRIMAUZ. Preparation of benzaldehyde, III, 417
- LAWES and GILBERT. Composition of meat, VIII, 262, 263
- LAWROW. Hydrolysis of oxyhæmoglobin, VIII, 544
- LAXA. Composition of the curd of sour milk, VIII, 122
- Rancidity of butter fat, II, 313
- LAXA, O. Analyses of milk chocolate, VI, 695
- LE BEL and HENNINGER. Bulb-tube distillation apparatus, I, 20; III, 233
- LE BON and NOEL. Hydrocyanic acid in tobacco smoke, VII, 463
- LE CLERE. Morphine, estimation of, IX, 507
- LE DOCTE. Sugar analysis, IX, 50
- LE ROY. Detection of sawdust in flour, I, 462
- LE SUEUR. Dihydroxystearic acid, preparation of, from oleic acid, II, 404
- Safflower oil, insoluble fatty acids of, II, 154
- See *Crossley*.
- LEA, M. C. Fractional distillation, I, 19
- LEACH. Butter, detection of annatto in, v, 663
- Maple products, adulteration of, with starch sugar, I, 389
- Milk, condensed, estimation of fat in, VIII, 213
- detection of colouring matters in, v, 659; VIII, 170
- Mustard, analyses of, VII, 107
- and LYTHGOE. Estimation of methyl alcohol in the presence of ethyl alcohol, I, 96
- Scale for reading Zeiss butyro-refractometer values, II, 282
- LEACH, ALBERT E. Coumarin, detection of, in vanilla essence, III, 522
- Meat, composition of, VIII, 268
- Microscopical examination of pepper and its adulterants, VII, 59
- LEATHER. Flax, effect of, on soil, II, 323, 324
- Linseed oil, percentage of, in linseed, II, 324
- Safflower oil, IX, 140
- See *Anschtz*.
- LEAVENSWORTH. See *Osborne*.
- LEBBIN. Resorcinol test for formaldehyde, I, 259
- LEBEAU and DAMIENS. Estimation of gaseous olefines, IX, 234
- Separation of hydrocarbons, IX, 230
- LEBEDEW, A. V. Fermenting enzyme in yeast, IX, 16
- LEBLANC. See *Janssens*.
- LECOMPTE. Test for silk, VIII, 646
- LECOMTE. Vanillin, III, 514
- detection of, IX, 307
- LEDDEHROSE. Composition of chitin, VIII, 671
- LEDENT. Coconut oil in butter fat, IX, 153
- Detection of saccharin, IX, 289
- LEEBOY. Determination of the tinctorial power of infusions of coffee, VI, 678
- LEEDS. Blown linseed oils, II, 362
- Butter, colouring matters in, II, 308
- Varnishes, II, 357
- LEEDS, A. R. Analysis of soap, II, 423
- VAN LEERSUM, P. Alkaloids in cinchona ledgeriana seeds, IX, 514
- function of, in plants, IX, 478
- LEES. Benzoyl derivative of camphor, IV, 206
- Methyl-nonylketone, IV, 190
- See *Power*.
- LEFEVRE and TOLLENS. Estimation of glucuronic acid, I, 399
- LEFFMANN. Abrastol, detection of, in milk, III, 260; VIII, 175
- Formaldehyde, removal of, from commercial formalin, I, 91
- and BEAM. Butter, detection of palm oil in, II, 310
- fat, saponification of, II, 294
- Wanklyn's test for, II, 299
- Esters, saponification of, I, 232
- Fats and oils, modification of the determination of the Reichert value of, II, 25
- Honey, adulteration of, with starch-sugar syrup, I, 387
- Invertase, use of, for the inversion of sugar in milk, I, 370
- Milk, estimation of fat in, VIII, 150
- separation of proteins in, VIII, 156
- Theobromine and caffeine in cocoa, VI, 700
- LEFFMANN, HENRY. Alcohols, neutral derivatives of, I, 227
- Milk, VIII, 139
- Soap, II, 415
- Vegetable acids, I, 485
- and LA WALL, CHARLES H. Special characters of essential oils, IV, 303
- LEFORT and THIBAUT. Effect of the presence of gum arabic on various reactions, I, 442
- LEGAL. Nitroprusside test for acetone, I, 105; VII, 402; IX, 577
- LÉGER. Aloes, detection of, in pharmaceutical preparations, VII, 149
- estimation of aloin in, VII, 147
- Klunge's test for, VII, 144
- Hordeine, VII, 36, 37
- Opium, assay of, VI, 426
- and ROQUES. Pilosine, IX, 537
- Pilosine, formation of anhydro-pilosine and pilosinine from, IX, 539
- LÉGER, A. E. Optical assay of quinine sulphate, VI, 524



- LÄGER, E.** Cinchona barks, composition of, vi, 481  
Coca leaves, assay of, vi, 349  
Quinine, estimation of, vi, 511
- LEHMANN.** Nicotine and sulphur compounds in cigars, vi, 252  
Tannins, estimation of, v, 85  
Vanillin, melting point of, ix, 308  
and **MÜLLER.** Assay of caffeine sodium salicylate, ix, 526  
Estimation of cinnamein in Peruvian balsam, ix, 295  
**STADLINGER.** Honey, commercial, estimation of cane sugar in, i, 387  
European, composition of, i, 384
- LEHNE.** Examination of dyed fibres, v, 486
- LEHNKERING.** Furfuraldehyde test for sesame oil, ii, 144
- LEIMDÖRFER.** Stearic acid formed in hydrogenation of oils, ix, 124
- LELLMAN.**  $\beta$ -Coniceine, vi, 216
- LEMAIRE.** Detection of artificial colouring matters in beeswax, ii, 262  
Estimation of antipyrine, vi, 44
- LENDRICH and MURDFIELD.** Caffeine, estimation of, in tea, vi, 609  
and **NOTTBOHM.** Caffeine in coffee, vi, 646, 657  
estimation of, ix, 526
- LENSSEN.** Estimation of ferricyanides, vii, 528
- LENZ.** Specific gravity and refractive index of glycerol, ii, 448, 450
- LENZ, W.** Detection of aloes, vii, 149
- LEONARD, N.** Detection of  $\alpha$ -nitronaphthalene in mineral lubricating oils, iii, 171
- LEONARD, N. and SMITH, H. M.** Optical activity of camphor, iv, 198  
Separation of formaldehyde from milk by distillation, i, 260
- LEPETIT.** Estimation of tannin, v, 89  
Sampling of tannin materials in barrels, v, 57
- LEPETIT, R.** Examination of dyed fibres, v, 486
- LÉPINE.** See *Caseneuve*.
- LERCH and SCHÄRGES.** Test for cocaine, vi, 323
- LERCHEN.** Xanthopuccine, vi, 574
- LERMER.**  $\beta$ -hop-bitter acid, vii, 165
- LESCHLY-HANSEN.** See *Bömer*.
- LÉSER.** See *Barbier*.
- LESSER.** Guaiacum test for blood, viii, 523
- LESSING, R.** Hydrocarbons, ix, 229
- LETSCHKE, E.** Conversion of oxyhæmoglobin to methæmoglobin, viii, 690
- LEU.** Assay of petroleum by distillation, iii, 50
- LEUSCHER.** See *Reichelman*.
- LEVENE.** Glycine, separation of, from the hydrolysis products of proteins, viii, 25  
Ichthulin, viii, 92  
Proteins, separation of mono-amino-acids formed by the hydrolysis of, viii, 23  
See *Fischer*.  
and **ALSBERG.** Vitellin, viii, 74, 92  
**BEATTY.** Glycyl-proline anhydride, viii, 471  
**BOUILLER.** Estimation of tryptophane, viii, 87  
**JACOBS.** Constitution of nucleic acids, viii, 72, 73
- LEVENE and MANDEL.** Nucleoprotein of spleen, viii, 92
- VAN SLYKE.** Glycine, separation of, from the hydrolysis products of proteins, viii, 25  
Mono-amino acids formed by the hydrolysis of proteins, separation of, viii, 24  
Picrolonates of amino-acids, ix, 562  
*d*-Valine and *d*-alanine, separation of, ix, 562  
Valine, leucine and isoleucine, separation of, viii, 25  
**WALLACE.** Glycyl-proline anhydride, viii, 471
- LEVENE, P. A.** Gelatoses, viii, 598  
Gelatone, preparation of, viii, 595
- LEVESIE, O.** Composition of coffee, vi, 644
- LEVI and ORTHMANN.** Tannin substitutes, ix, 409
- LEVI-MALVANO.** See *Carlinfanti*.
- LEVINSTEIN.** Direct estimation of *o*-xylene in commercial xylene, iii, 219, 220
- LEVISON.** See *Fuld*.
- LEVY, P.** Melting point of abietic acid, iv, 22
- LEWCOCK.** See *Pickard*.
- LEWES.** Dilution of acetylene with other gases, iii, 10
- LEWIN.** Specific gravity of Russian and Siberian butters, ii, 286  
**MIETHE and STENGER.** Spectrum of hæmoglobin, viii, 514, 515  
and **ROSENSTEIN.** Hæmin test for blood stains, viii, 575
- LEWINSKY.** Detection and isolation of aspartic acid, vii, 241
- LEWIS.** Hippuric acid, ix, 569  
See *Hake*.
- LEWIS, E. W.** India-rubber, rubber substitutes and gutta-percha, iv, 105; ix, 320
- LEWIS, RICHARD H.** See *Charles S. Reese*.
- LEWITE, A. and HAUSER, O.** Titanium, tetravalent, behaviour of, with phenols, naphthols and phenolcarboxylic acids, ix, 272
- LEWITH.** Precipitability of animal proteins by salts, viii, 77
- LEWKOWITSCH.** Acetin, estimation of, ii, 460  
Acrylic acid series of acids, ii, 375  
Almond oil, ix, 130  
butyro-refractometer values for, ii, 102  
detection of peach-kernel and apricot-kernel oils in, ii, 104  
phloroglucinol test applied to, iii, 422  
solidifying point of the mixed fatty acids from, ii, 103  
sweet, French, iii, 420  
Apricot-kernel oil, ii, 105; ix, 130  
Arachis oil, ix, 126  
fatty acids from, ii, 93, 98  
Beeswax, Weinwurm's test for, ii, 257  
Blown oils, analyses of, ii, 362, 363, 364, 365  
Cacao butter, constants for, vi, 702  
detection of tallow in, ii, 180  
dika fat as a substitute for, ii, 179  
effect of exposure on, ii, 177  
solidifying point of the mixed fatty acids from, ii, 178



- LEWKOWITSCH.** Candle nut oil, II, 149  
 Carnaúba wax, acetyl value for, II, 271  
 Castor oil, composition of, II, 160  
 Cerotic acid, II, 243  
 Cholesterol, estimation of, II, 491  
   iodine value for, II, 480  
 Coast cod oil, II, 214  
 Coconut oil, composition of, II, 188  
   free fatty acid in, II, 187  
   solidifying point of the mixed fatty acids  
   from, II, 188  
 Codliver oil, colour test for, II, 220  
   solidifying points of mixed fatty acids  
   from, II, 215  
 Colophony, constants for, IV, 26  
 Cottonseed oil, II, 132  
   nitric acid test for, II, 138  
 Cresylic acid sheep dips, estimation of fatty  
   acids in, III, 330  
 Croton oil, constants for, II, 173  
 Curcas oil, II, 174  
 Driers, II, 360  
 Dynamite glycerin, II, 471  
 Fats, oils and waxes, determination of the  
   acetyl value for, II, 33, 35  
   and oils, determination of the bromine  
   value of, II, 27  
   theory of the reactions of the Hübl proc-  
   ess for the determination of the  
   iodine value for, II, 31  
 Fatty acids, acetyl value of, II, 33, 389  
   mean molecular weight of, II, 378  
 Glycerol, estimation of, II, 463, 466, 477  
 Hemp seed oil, titer test of mixed fatty acids  
   from, II, 151  
 Jamba oil, II, 131  
 Japanese wood oil, IX, 144, 145  
 L-Lactic acid, VII, 449  
 Linoleum, II, 362  
 Linseed oil, adulteration of, II, 342, 343  
   ash from, II, 332  
   boiling of, II, 347, 354, 355  
   cameline oil in, II, 132  
   composition of, II, 330  
   insoluble bromides from, II, 29, 337  
   saponification value for, II, 334  
   solidification of, II, 331  
   solidifying point for the fatty acids from,  
   II, 350  
   titer test of fatty acids from, II, 337  
   use of candle nut oil as an adulterant of, II,  
   148  
 Maize oil, solid fat deposited by, on standing,  
   II, 140  
   titer test for the mixed fatty acids from, II,  
   141  
 Olive oil, composition of, II, 107  
   iodine value for, II, 113  
   solidifying point of the mixed fatty acids  
   from, II, 108  
 Palmitic acid in palm oil, II, 185  
   preparation of, from oleic acid, II, 404  
 Palm-nut oil, solidifying point of the mixed  
   fatty acids from, II, 196
- LEWKOWITSCH.** Palm oil, iodine value for the  
 mixed fatty acids from, II, 184  
 Paraffin scale, determination of the solidify-  
   ing point of, III, 195  
 Peach kernel oil, II, 105  
 Phenols, estimation of, in soap, II, 428  
 Poppyseed oil, titer test of mixed fatty acids  
   from, II, 153  
 Rape oil and cottonseed oils, distinction  
   between, II, 370  
   solidifying point for the fatty acids from,  
   II, 124  
 Resins, effect of heat on, IV, 11  
 Rosin, estimation of, in crude oils, II, 78  
 Sesame oil, II, 141, 142  
 Shark-liver oil, II, 223  
 Sperm oil, alcohols from, II, 234  
   ether residue from, II, 234  
   fatty acids from, II, 235  
 Spermaceti, commercial, II, 275  
 Stearic acid in beef tallow, II, 208  
   from butter fat, II, 280  
 Tallow, solidifying point of the fatty acids  
   from, II, 209  
 Triglycerides, saponification of, II, 13  
 Turkey-red oil, examination of, II, 168, 170  
 Varnishes, II, 357  
 Waxes, ratio number for, II, 254  
 Wool-fat, II, 496, 497  
   composition of, II, 495, 501  
   estimation of free fatty acids in, II, 496  
   saponification of, II, 499  
 Wool-grease, distilled, II, 502  
 Wool-wax in beeswax, II, 261  
 See *Benedict*.
- LEWY, L.** Separation of *o*- and *p*-toluidine, VI, 67  
**LEY.** Detection of invert sugar in commercial  
 honey, I, 386  
**LEYBOLD.** Estimation of cyanogen in coal gas,  
 VII, 457  
 See *Moldenhauer*.
- LEYS.** Action of ferric chloride and hydrogen  
 peroxide on saccharin, III, 431  
 Detection of annatto in milk, VIII, 169
- LIDDLE.** See *Barnes*.
- LIDOFF, A. P.** Estimation of hydrogen, IX, 237
- LIDOW.** Investigation of the elaidin reaction for  
 oils, II, 40
- LIDOW, A. P.** Cyanamide salts, commercial, IX, 589
- LIEBEN, A.** Detection of alcohol in chloroform, I,  
 278
- LIEBERMANN.** Cocamine, VI, 340  
 Guaiacum test for blood, VIII, 523  
 Phenol, detection of, III, 297  
 Silk, test for, VIII, 647  
 See *Feuerstein*.
- and **BAGARSKY.** Changes in the hydrogen ion  
 concentration of acidic and basic solu-  
 tions of proteins, VIII, 88
- GIESEL.** Preparation of ecgonine, VI, 337  
 $\alpha$ - and  $\beta$ -quinovin, VI, 482
- STUDER.** Detection of magenta in orchil  
 and cudbear, V, 429
- TAUCHERT.** Formula of catechin, V, 29

- LIEBERMANN, C.** Preparation of cochineal carmine, v, 423
- LIEBERMEISTER.** Blood nucleoprotein, viii, 92
- LIEBIG.** Cinchonidine, detection of, in quinine sulphate, vi, 520  
Condenser, i, 18  
Cyanides, estimation of, vii, 481  
Extract of meat, viii, 390  
Potassium cyanide, preparation of, vii, 473  
Yeast, chemical composition of, i, 208  
and **PASTEUR.** Yeast-cellulose, i, 209  
and **WOEHLER.** Decomposition of amygdalin, vii, 463
- LIEBMANN.** Estimation of  $\beta$ -naphthol in the presence of  $\alpha$ -naphthol, iii, 257
- LIEBNER.** See *Schulze*.
- LIEBREICH.** Benzoyl-pseudotropine, vi, 341
- LIEBRICH.** Lanolin, ii, 502
- LIECHTI and SUIDA.** Aniline black, v, 312
- LIESCHING.** Estimation of potassium ferricyanide, vii, 528
- LIFSCHITZ, J.** Peppermint oils, iv, 371
- LIFSCHÜTZ.** See *Darmstädter*.
- LIFSCHUTZ and GRETHE.** Oxycholesterol, digitonide of, ix, 547
- LIKIERNIK.** Lupeol, ii, 488  
Paraphytosterol from French beans, ii, 488  
Phytosterol from *pisum sativum*, ii, 485  
See *Schulze*.
- LILLIE.** Molecular weight of proteins, viii, 77
- LIMON.** Guaiacum test for blood, viii, 523
- LINDE.** Bitter-almond water, iii, 427  
Estimation of alkaloids, vi, 180, 183  
See *Tröger*.
- LINDENMEYER.** Phytosterol from peas and various oils, ii, 485
- LINET.** Flour, evaluation of, ix, 593  
See *Girard*.  
and **AMMAN.** Action of rennet-enzyme, viii, 129  
**AMMAUN and BRUGIÈRE.** Analyses of French cheeses, viii, 253
- LINDNER.** Yeast, microscopical examination of, i, 220  
occurrence of melibiase in, i, 211  
and **KROEBER.** Maltase in yeast, i, 211  
**WILL.** Cell wall of yeast, i, 206
- LING.** Invert sugar in brewing, ix, 8  
Malt, diastatic activity of, i, 136  
extracts, analyses of, ii, 145  
Saccharin, purification of, iii, 428  
Starch, structure of, i, 379  
Sugars, estimation of, by Soxhlet's method, i, 322  
and **BAKER.** Estimation of reducing sugar, ix, 24
- EYNON and LANE.** Solution densities of sugars, ix, 19, 20  
and **JONES.** Invert sugar and saccharose, estimation of, ix, 9  
Malt wort, determination of the reducing power of, i, 142  
Wines, estimation of reducing sugar in, i, 171
- LING and POPE.** Determination of the index of refraction of beer, i, 156
- RENDLE.** Determination of the reducing power of malt wort, i, 142  
Estimation of reducing sugar in wines, i, 171  
and **JONES, G. C.** Use of ferrous thiocyanate as an indicator in the estimation of sugar by Soxhlet's method, i, 321
- LINK and MAECKEL.** Detection of hydrocyanic acid, vii, 479
- LINKE.** Estimation of salicylic acid, ix, 303, 306
- LINNEMANN.** Separation of propionic acid from its lower homologues, i, 522
- LINOSSIER.** Production of active lactic acids, vii, 449
- LINTNER.** Cereals, polarimetric estimation of starch in, i, 424  
Hops, detection of sulphuring in, vii, 183  
estimation of resins in, vii, 167, 177; ix, 554  
and **BARTH.** Lupulinic acid, vii, 167  
**BUNGNER, A.**  $\alpha$ -hop acid, vii, 166  
**SCHNELL.** Humulone, vii, 166
- LINTON.** Composition of asphalt, iii, 61, 63  
Fractional separation of the constituents of asphalt, iii, 86
- LIPOWITZ.** Jelly strength of glue, viii, 607
- LIPPERT.** Boiled linseed oil, adulteration of, ii, 356  
Driers, ii, 359, 360  
Drying of oils, effect of external influences on the, ii, 347  
Liebermann-Storch reaction for the detection of rosin in linseed oil, ii, 341  
Linseed oil, free fatty acids in, ii, 333  
use of, for varnish, etc., ii, 328  
and **REISSIGER.** Analysis of copals, iv, 55
- LIPPICH.** Polarimeter, i, 42, 45
- LIPPMAN.** Lævulose and cane sugar, specific gravity of corresponding solutions of, i, 294  
Phytosterol from beet juice, ii, 485  
Vanillin, presence of, in the wood of trees, iii, 514
- LIPPMAN, E. and POLLAK, J.** Behaviour of solid hydrocarbons with benzal chloride, iii, 280
- LISSIZIN.** Formation of azelic acid from horn, viii, 676
- LIST.** See *Beckurts, Fahlberg*.
- LITTERSCHIED, F. M. and GUGGARI, P. B.** Available oxygen in peroxide soaps, ix, 208
- LITTLE.** Estimation of citral, ix, 338
- LITTLEBURY.** See *Pickard*.
- LIVACHE.** Drying of oils, ii, 36, 343
- LIVERSEEGE.** Butyro refractometer values for codliver oil, ii, 218  
seal oil, ii, 227  
Fish-liver oils, ii, 221  
Specific gravity of mixtures of ethyl alcohol and water at various temperatures, i, 122  
Whale oil, ii, 229
- LIVERSEEGE, J. P.** Tincture of myrrh, estimation of the alcoholic strength of, iv, 102

- LIVERSEGE, J. F. and ELSDON. Drying of linseed oil, IX, 193
- EVERS. Estimation of benzoic acid in milk, IX, 285
- LIVERSIDGE. Piturine, VI, 229
- LLOYD. Extraction of indigo, IX, 430
- See *Green*.
- LLOYD, P. J. Analyses of condensed milk, VIII, 210
- Manufacture of English cider, I, 187
- LLOYD, J. U. Caffeine and caffeine citrate, separation of, VI, 590
- Berberine sulphate, VI, 560
- Opium, assay of, VI, 421
- Strychnine, oxidation test for, VI, 451
- LLOYD, J. U. and C. G. Lobeline, VI, 224
- LOCQUIN. See *Barbier*.
- LOEBELL, H. Asphalt, natural and petroleum, separation of, IX, 245
- LOEBISCH. Analysis of mucin, VIII, 628
- and SCHOOP. Melting point of strychnine, VI, 442
- LÖHR, H. Estimation of camphor in camphor oil, IV, 323
- LÖRCHER. Compounds which retard rennet coagulation, VIII, 130
- Rennet enzyme, VIII, 126
- LOESCH, A. Estimation of volatile alkaloids, VI, 207
- LOEVENHART. Addition of soluble calcium salts in the action of rennet on casein, VIII, 127
- See *Amberg*.
- LOEW. Catalase, VIII, 691
- in yeast, I, 213
- Enzyme of tobacco leaves, VIII, 15
- See *Nageli*.
- LOEWE. Determination of the melting point of fats by the formation of an electric circuit, II, 54
- LÖWE. Anhydride of quercitannic acid, V, 26
- Formula of hydrated tannic acid of oak-bark, V, 26
- LÖWENHARDT. See *Schmidt*.
- LÖWENTHAL. Oxidation method of tannin assay, V, 60
- LÖWY and NEUBERG. Formation of cadaverine in the urine in cystinuria, VII, 348
- LOGAN. See *Vallé*.
- LOHMANN. See *Van Romburg*.
- LOHRMANN. Differences between natural, artificial and synthetic camphor, IV, 201
- LONDON and SOLOWJEW. Hydrolysis of proteins, VIII, 469
- LONG. Casein, action of acids on, VIII, 122, 124
- Turpentine oil, rotation of, IV, 410, 411
- LONG, J. H. Ammonia, estimation of, in pyridine, VI, 137
- use of, in conjunction with phenolphthalein, III, 553
- Petroleum and turpentine oil, flash-points and densities of mixtures of, IV, 410
- Polarimeters, I, 46
- Turpentine oil, American, IV, 401
- rotation of, IV, 406
- LONG, J. H. Turpentine oil, specific gravity of, IV, 408
- vapour density of, IV, 408
- and RIBAU. Melting point of pinene hydrochloride, IV, 181
- LOOMIS. Coal tar colours, detection of, in food, V, 643
- meat products, VIII, 385
- reactions of, V, 634
- LORETZ. See *Caesar*.
- LOSSEN. Hygiene, VI, 342
- Phthalic acid, melting point of, III, 543
- anhydride, boiling point of, III, 544
- LOTT. See *Matthews*.
- LOTT, F. E. Decomposition of salicylic acid on standing, III, 470
- LOTTER. Extraction of linseed oil from paint, II, 329
- Use of poppyseed oil for the manufacture of pigments, II, 152
- LOVATT, S. Flour, moisture in, IX, 593
- LOVIBOND, J. W. Determination of the colour of malt-wort by the Lovibond tintometer, I, 135
- Loss of colour of dyed fabrics when exposed to light, V, 484
- LOW. Butter, detection of colouring matters in, V, 664
- Copper, estimation of, in cuprous oxide precipitate, VIII, 375
- Reducing sugars, estimation of, IX, 41
- LOWE. See *Senior*.
- LOWENSTEIN, A. Meat extracts, estimation of mocatine in, VIII, 397
- estimation of moisture in, VIII, 405
- Starch, estimation of, in sausage, VIII, 373
- LOWRY, T. MARTIN. Camphor,  $\beta$ -derivatives of, IV, 202
- Essential oils, hydrocarbons of, IV, 163
- ketones of, IV, 189
- Gas regulators and thermostat, I, 53
- Muta rotation, I, 315
- Polarimetry, use of the Bastian mercury lamp in, I, 43
- Specific gravity of liquids, determination of, I, 7
- Thermostat of, I, 6, 29, 52
- See *Bousfield*.
- See *E. F. Armstrong*.
- LUBBERGER. Estimation of cyanogen in spent gas purifying mass, VII, 520
- LUCIUS. See *Meister*.
- LUDDENS, H. Preparation of phthalic acid, III, 542
- LUDWIG. Butter, refractive index of the fatty acids from, II, 283
- Cocoa husks and cocoa, analyses of, VI, 696
- Coffee ash, composition of, VI, 653
- Uric acid, estimation of, VII, 368
- LÜCK, E. Anthraquinone test for anthracene, III, 282
- LÜCKER. See *Döbner*.
- LÜDY. Composition of Siam and Sumatra beans, III, 449
- See *Tschirch*.

- LUEHRIG.** Estimation of ferrocyanides in spent gas purifying mass, VII, 516
- LUERS, H.** Test for arachis oil, IX, 129
- LUERSSEN and KÜHN.** Bacillus of fermented milk, VIII, 224
- LÜTKE, S.** o-phenacetin, detection of, VI, 99  
detection of diaminophenols in, VI, 100
- LUFF.** Tin in canned cherries, VIII, 339  
See *Wright, Alder*.
- LUHRIG, H.** Cocoa husks, VI, 696
- LUMIÈRE and SEYEWETZ.** Compounds of gelatin with formaldehyde and quinone, VIII, 592
- LUNDELL, G. E. F. and BRIDGMAN, J. A.** Hydrocyanic acid and cyanides, estimation of, IX, 586
- LUNGE.** Acetone extraction of rubber, IV, 124  
Benzene, commercial, estimation of available benzene in, III, 207  
Benzols, analysis of, IX, 260  
and coal-tar naphthas, distillation of, III, 289  
detection of carbon disulphide in, III, 226  
Benzyl chloride, detection of, in benzaldehyde, III, 423  
Cinnamic acid, detection of benzoic acid in, III, 437  
estimation of, III, 438  
Formulæ for obtaining specific gravity by means of Baumé's hydrometer, I, 8  
Naphthalene, sensitiveness of, to air and light, III, 250  
Potassium hydrogen tartrate, estimation of by Oulman's method, I, 545  
p- and o-toluidine, densities of mixtures of, VI, 69  
and **BEBIE.** Nitrocellulose, III, 561  
**CEDERCREUTZ.** Assay of calcium carbide, III, 11  
**WEINTRAUB.** Estimation of unnitrated fibre in gun cotton, III, 567  
Solubility of nitrocellulose, III, 565
- LUNGWITZ.** See *Schweitzer*.
- LUPPO-CRÄMER.** Detection of traces of chlorides in gelatin, VIII, 615
- LUSK.** See *Gephart*.
- DE LUYNES.** Preparation of azolitmin, V, 429
- LUZ.** See *Tschirch*.
- LYFORD.** See *Woodman*.
- LYON, W.** Solvent for free salicylic acid in bismuth salicylate, III, 490
- LYONS.** Aconite, assay of, VI, 281  
Alkaloids, behaviour of, with Mayer's reagent, VI, 193  
Belladonna and its preparations, assay of, VI, 316  
Benzoic acid, estimation of, in benzoates, IX, 283  
Ipecacuanha, assay of, VII, 44  
percentage of alkaloids in, VII, 48  
Morphine, estimation of, IX, 505  
Stramonium seeds, alkaloid in, VI, 319
- LYONS, A. B.** Cocaine, detection of impurities in, VI, 325  
estimation of, in coca leaves, VI, 350  
tests for, VI, 323
- LYONS, A. B.** Colchicine, estimation of, VII, 11  
Hydrastine, tests for, VI, 566, 567
- LYTHGOE.** Castor oil, butyro-refractometer values for, II, 161  
rotation of, II, 160  
Codliver oil, butyro-refractometer values for, II, 218  
Milk, composition of, VIII, 143  
detection of the addition of water to, VIII, 165  
coal-tar colours in, VIII, 170  
Neatsfoot oil, II, 200, 201  
See *Leach*.
- and **MARSH.** Detection of benzoic acid in coffee, IX, 282  
Preservatives in coffee extracts, IX, 532
- M**
- MABEN.** Volumetric estimation of hydrastine, VI, 568
- MABEN, T.** Analysis of commercial gallotannic acid, V, 22
- MABERY.** Petroleum, Californian, III, 41  
nitrogen in, III, 39  
Canadian, hydrocarbons in, III, 41  
crude, estimation of sulphur in, III, 52  
Ohio, III, 42  
Pennsylvania, III, 41  
and **QUAYLE.** Sulphur compounds in Canadian petroleums, III, 40  
**SMITH.** Sulphur in petroleum, III, 40  
**WILLIAMS, J. H.** Comparative lubricating values of hydrocarbon series, III, 144
- MCABEE.** Estimation of sodium benzoate, IX, 284
- MCCARTHUR.** Estimation of olefines in liquid hydrocarbons, III, 5
- MCBRYDE.** Ham curing, VIII, 356
- MCBRYDE, C. N.** Canning of meat, VIII, 330
- MCCANDLESS, J.** Turpentine oil, adulteration of, IV, 414  
Detection of petroleum products in, IV, 416  
Wood, IV, 424, 425
- MCCRAE.** Test for salicylic acid, IX, 300
- MCBELROY.** See *Bigelow*.
- MCFADDEN.** Test for lead in commercial tartaric acid, IX, 101
- MCGILL, A.** Examination of turpentine oil, IV, 422  
Specific gravity of infusions of coffee and chicory, VI, 660, 661
- MCILHINEY, P.** Ink, printing, estimation of hard gums in, IX, 459
- Linseed oil, boiled, II, 354**  
bromine value for, II, 336  
constants of, II, 350
- Oils, determination of the bromine substitution value for, II, 27**
- Olefines and aromatic hydrocarbons, estimation of, IX, 233**
- Rosin oil, estimation of, in mineral lubricating oil, III, 174**
- McKEE.** Paper and paper-making materials, IX, 80

- McLAUCHLAN. Lactic acid, commercial, valuation of, VII, 441  
preparation of, from sugar, VII, 430
- McLELLAN. See *Davies*.
- McMILLAN. See *Rabe*.
- MACAGNO. Estimation of tannins, v, 85
- MACAGNO, H. Estimation of carbon disulphide in commercial benzols and naphthas, III, 227
- MACAGNO, J. Fermentation of lemon juice, I, 955
- MACARA, T. Analyses of condensed milk, VIII, 211
- MACDONALD, J. W. Average composition of the sulphated ash of cane and beet sugar, I, 349
- MACELROY and KRUG. Specific gravity of acetone, I, 105
- MACEWAN, P. Camphor oils, IV, 321  
Determination of free acid in spirit of nitrous ether, I, 244
- MACFARLANE, T. Coffee, adulteration of, VI, 671  
and chicory, specific gravity of infusions of, VI, 661  
estimation of fat in, VI, 656  
Tincture of myrrh, solids in, IV, 103  
Turpentine oil, IV, 425  
refractive index of, IV, 406  
specific gravity of, IV, 408
- MACGREGOR. See *Frankland*.
- MACH. Composition of colophony, IV, 22  
Melting point of abietic acid, IV, 22
- MACKAY. Apparatus for the determination of the spontaneous combustion of oils, II, 38  
Cloth-oil tester, II, 512
- MACLAGAN, H. Test for the purity of cocaine hydrochloride, VI, 332
- MACMUNN. Occurrence of hæmatoporphyrin in the integuments of molluscs and echinoderms, VIII, 554
- MADSEN. See *Buntzen*.
- MAECKEL. See *Link*.
- MÄRCKER. See *Behrend*.  
and MORGEN. Estimation of starch, I, 423  
SCHULZE. Analyses of raw wool, VIII, 682
- MAGALHÃES. Reaction of cytisine, VII, 14
- MAGNUS-LEVY. Estimation of  $\beta$ -hydroxybutyric acid in urine, VII, 404
- MAGUIO. See *Labbe*.
- MAHLA. Berberine, VI, 552
- VON MAHLES. Detection of saccharin in foods and beverages, III, 433
- MAI and RATH. Estimation of morphine, VI, 433
- MAIN. Refractometer values for sugar solutions, IX, 21
- MAIRET and COMBENALE. Toxicology of colchicum, VII, 11
- MAISCH. Detection of nitrobenzene in essential oil of bitter almonds, III, 425  
See *Harrison*.
- MAISCH, J. M. Adulteration of saffron, v, 419
- MAJERT. Manufacture of piperazine, VII, 198  
and SCHMIDT. Identity of spermine, piperazine and piperazidine, VII, 197
- MAJERT and SCHMIDT. Non-identity of piperazine and Schreiner's spermine, VII, 203  
Piperazine, VII, 198
- MAKIN. See *Fresenius*.
- MAKOSHI. Japaconitine, VI, 266  
Jesaconitine, VI, 273
- MAKRINOFF. Bacillus of fermented milk, VIII, 224
- MALACARNE. Colour tests of oils, IX, 122  
See *Calvi*.
- MALAGNINIANA ARMANNI. Sesame oil, II, 142
- MALAGUIN. Test for strychnine, VI, 453
- MALET. See *Milliau*.
- MALJEAN. Detection of frozen meat, VIII, 351
- MALLINCKRODT and DUNLAP. Composition of meconates contaminating morphine, VI, 421
- MALLMANN. Separation of water from tars, III, 14
- MALY. Composition of colophony, IV, 22  
See *Hammarsten*.
- MAMELLE. Use of alkali cyanide as an insecticide, VII, 472
- MANCUSO-LIMA and SCARLATA. Estimation of glycerol in wines, I, 168
- MANDEL and NEUBERG. Test for glycuronic acid, VII, 398  
See *Levens*.
- MANDEL, J. A. Animal acids, VII, 357
- MANFELD. Preservative for cheese, VIII, 249
- MANGINI, F. Dragendorff's reagent for alkaloids, VI, 190
- MANGOLD. Estimation of hydrocarbons in beeswax, II, 258, 260  
Use of hydrogen peroxide in the estimation of glycerol, II, 458
- MANN. Finmark codliver oil, II, 214  
Oxydase in tea, VI, 598  
Tea, IX, 528
- MANN, E. W. Commercial copaiba, IV, 87
- MANN, P. and TOLLENS, B. Estimation of glycuronic acid, VII, 398
- MANNHARDT. Drying test for linseed oil, IX, 194
- MANNICH and SCHWEDES. Pantopon, IX, 502
- MANNICH, C. and SCHWEDES, L. Test for quinine, IX, 516
- MANNING. Hydrates of an ethyl ester of gallo-tannic acid, v, 18
- MANUFACTURING CHEMISTS ASSOCIATION, U.S.A. Baumé hydrometer, I, 9, 11
- MAPURGO. Detection of nitrobenzene in essential oil of bitter almonds, III, 425
- MAQUENNE. Estimation of reducing sugars, IX, 625
- MARARO, P. Quinine tannate, VI, 530
- MARCHADIER. Detection of benzoic acid in butter, IX, 282
- MARCHLEWSKI. Chlorophyll, v, 638  
See *Schunck*.
- MARCILLE, R. Detection of cottonseed oil in olive oil, IX, 132
- MARCK.  $\beta$ -Amyrin, II, 488  
Coca leaves, assay of, VI, 349  
Paraffin, estimation of, in asphaltum, IX, 245

- MARCKWALD. See *Frank*.  
 and VON DROSTE-HUELSHOFF. Separation of amines, VI, 4  
 FRANK. Analysis of gutta-percha, IV, 160  
 HALTZ. Manufacture of piperazine from aromatic disulphone-piperazides, VII, 198  
 MARCUSSEN. Asphalt, estimation of water in, III, 74  
   natural, estimation of, IX, 245  
   and petroleum, separation of, IX, 245  
 Blown oils, IX, 201  
 Lubricating greases, determination of the water in, III, 179  
 Paraffin wax, identification of, IX, 238  
 Rape and cottonseed oils, distinction between, II, 370  
 Triglycerides, saponification of, II, 13  
 See *Hinrichsen*, *Holde*.  
 and HINRICHSEN. Estimation of mineral matter in rubber, IX, 323  
 MEYERHEIM. Hydrogenation of oils, IX, 124  
 SCHILLING. Digitonin test for butter, IX, 164  
   Separation of phytosterol and cholesterol in fats, IX, 118  
 MARCUSSEN, J. and WINTERFELD, G. Copals, determination of the acid value of, IV, 56  
   Resin acid, estimation of, in driers, IV, 35  
   Resins, estimation of the acid value of, IV, 9  
   Turpentine, estimation of mineral oil in, IV, 417  
 MARDEN. Extraction of vanillin, IX, 308  
 MARFORI. Solubility of guaiacol in water, III, 345  
 MARGOSCHES. See *Donath*.  
 MARGUERITE and SOURDEVAL. Preparation of barium cyanide, VII, 475  
 MARIE, T. Free acids in beeswax, II, 243  
 MARINO-ZUCO. Phytosterol-like substance from chrysanthemum flowers, II, 488  
   Separation of neurine from vegetable alkaloids, VII, 275  
 MARISCHLER. Sulphurous acid in wines, I, 174  
 MARKOWNIKOFF and OGLOBINI. Caucasian petroleum, III, 42, 43  
 MARMÉ. Physiological action of arecoline, VI, 210  
 MARPMANN. Detection of colouring matters in flesh foods, V, 650  
 MARQUARDT. Examination of mixtures of dyes, V, 441  
   See *Einhorn*.  
 MARRIOTT. Acetone, estimation of, IX, 577  
   Blood, acetone in, IX, 576  
    $\beta$ -Hydroxybutyric acid, estimation of, IX, 578  
   See also *Shaffer*.  
 MARSDEN, P. H. Guarana, VI, 684  
 MARSH. See *Lythgoe*.  
 and GARDNER. Rotation of turpentine oil, IV, 411  
   STRUTHERS. Estimation of acetophenone, III, 428  
 MARSHALL. Acetone, commercial, assay of, I, 109  
   Glycocholic acid, preparation of, VII, 411  
   Modern explosives, III, 559  
   Nitroglycerin explosives, moisture in, III, 592  
   vapour tension of, III, 570  
 MARTELLI. Detection of poivrete, VII, 68  
 MARTENS. Modification of Abel's closed oil tester, III, 124  
 MARTIN. Butter, detection of colouring matters in, V, 663  
   See *Chick*.  
 and MOOR. Asafetida, IV, 94  
   tincture of, IV, 95  
 CLAUDE. See *Truchon*.  
 MARTIN, S. H. C. Separation of peptones from other proteins, VIII, 396  
 MARTINDALE. Digitalis tincture, test for, IX, 546  
 MARTINEZ-STRONG. Specific gravity of aqueous solutions of glycerol, II, 448  
 MARTINON. Detection of dyes on silk, V, 486, 511  
 MARTINOTTI and CORNELIO. Commercial bismuth salicylate, III, 489  
 MARX. See *Willstätter*.  
 MARZOCCHI. See *Carlinfanti*.  
 MASKELYNE. Melting point of lead palmitate, II, 399  
 MASON. See *Gill*.  
 and STEELE. Composition of Fehling's solution, I, 318  
 MASON, A. H. Effect of alcohol on the specific gravity of chloroform, I, 280  
 MASSOL. Estimation of protocatechuic acid, III, 512  
 MASSOT. Microscopical and physical characters of artificial silk, VIII, 663  
 MASTBAUM. Detection of salicylic acid in urine, III, 477  
   See *Cordoso*.  
 MATEGCZEK and SCHEIBLER. Baumé hydrometer, IX, 4  
 MATHEWSON. Separation and identification of oil-soluble colours in foods, V, 666  
 MATHEWSON, W. E. Colouring matters in foods, IX, 449, 452  
   Estimation of dyestuffs, IX, 419  
 MATRAS, L. Substitution derivatives of fluorescein, V, 293  
 MATTHAIPOULOS. Basicity of casein, VIII, 124  
 MATTHES and RAMMSTEDT. Hydrastine, gravimetric estimation of, VI, 571  
   Morphine, estimation of, VI, 433  
   Nux vomica, estimation of the total alkaloids in, VI, 470  
   Picrolonic acid as a reagent for alkaloids, VI, 187  
   Pilocarpine, estimation of, VII, 53  
 and ROHDICH. Cacao butter, acid value for, VI, 718  
   composition of, II, 177  
   Beans, soluble silica in, VI, 704  
 MATTHEWS. Arbacin, VIII, 91  
   Removal of mineral oils before dyeing, II, 511  
 and LOTT. Forcing test for beers, I, 164  
 MATUCHEK. Soluble Prussian blue, VII, 526  
 MAUCH. Examination of resins, IV, 8  
 MAUMENÉ. Rise of temperature on the addition of sulphuric acid to fixed oils, II, 58  
 MAUPY, L. Detection of castor oil in copaiba balsam, IV, 89



- MAURENBRECKER and TOLLENS. Carbohydrates in tea, VI, 629
- MAXWELL. See *Schultze*.
- MAXWELL, W. Cattle foods, detection of choline and betaine in, VII, 278  
Lecithin in eggs, VII, 283
- MAY, R. T. and DREAPER, W. P. Valuation of commercial malt extracts, VIII, 689
- MAYER. Detection of wool grease in tallow, II, 212  
See *Clausnitzer*.
- MAYER, A. Composition of chicory root, VI, 674
- MAYER, E. W. See *F. W. Semmler*.
- MAYER, F. F. Potassium mercuric iodide as a reagent for alkaloids, VI, 191
- MAYER, L. Detection of cottonseed oil or stearine in tallow, II, 212
- MAYRHOFER. Glycogen, estimation of, in horse flesh, VIII, 378  
Hydrastine, detection of, IX, 522  
Starch, estimation of, in sausage, VIII, 373  
See *Donath*.
- MAYS, T. J. Poisoning by brucine, VI, 465
- MEACHAM. See *Briant*.
- MECKE and WIMMER. Ptomaines which give the strychnine oxidation test, VI, 452
- MEDICUS and WELLENSTEIN. Effect of bleaching on the constants of beeswax, II, 246
- MEDIN, O. Estimation of alkaloids in cinchona barks, VI, 489
- MÉHU, A. C. Detection of indoxyl-sulphuric acid in urine, VII, 256
- MEIDINGER. See *Hell*.
- MEIER. See *Hersog*.
- MEIGEN and WINOGRADOFF. Halogen values of fatty acids, IX, 120
- MEILLIÈRE, G. Assay of kola, IX, 532
- MEISENHHEIMER. Formation of lactic acid from galactose, VII, 430  
See *Buchner*.
- MEISSEL. Hydrolysis of carbohydrates, I, 297
- MEISSL. Determination of the fermenting power of yeast, I, 222, 223  
Modification of Reichert's value for fats and oils, II, 23  
and HILLER. Formulae and table of factors for the estimation of small quantities of invert sugar, I, 329
- MEISSNER. Estimation of lactic acid in muscle extractive, IX, 608
- MEISTER. Driers, II, 360  
Linseed oil, iodine value for, IX, 189  
Resinates, commercial lead and manganese, IV, 33  
See *Wilhelm*.
- LUCIUS and BRÜNING. Anthraquinone test for anthracene, III, 282  
Patent blue, V, 243
- MELDOLA, R. Eikonogen, VI, 126
- MELLANBY. Extraction of animal globulins, VIII, 61  
Identification of proteins by their solubilities VIII, 76
- MELLOR. Estimation of cyanates, VII, 540
- MELSENS. Tobacco smoke, VI, 251
- MELZER. Detection of nicotine, VI, 239
- MENCKE. See *Jackson*.
- MENDEL. See *Osborne*.
- MENDELÉEF. Ethyl alcohol, specific gravity of, I, 110  
ether, specific gravity of, I, 227  
Glycerol, boiling point of, II, 447  
Kerosene, specific gravity of, III, 129
- MENGE. Santonin, VII, 152
- MENKE, A. E. Tin in canned foods, VIII, 338
- MENON. Tea seed oil, IX, 134
- MENSCHUTKIN. Detection of amines by acetylation, VI, 5
- MENTZEL. See *Arnold*.
- MENZIES. Bile, analyses of, IX, 579
- MERCK. Alkaloids of *sabadilla*, VII, 69  
Cocaine ethyl ester, VI, 327  
Hydrastine tartrate, VI, 572  
Hydrastinine hydrochloride, VI, 573  
Indian opium, test for, VI, 404  
Laudanine, colour reaction of, with ferric chloride, VI, 367  
Pseudohyoscyamine, VI, 298  
Tropine, artificial, VI, 301
- MERCK, C. E. Distillation of ecgonine with barium hydroxide, VI, 337
- MERCK, E. Ethyl alcohol, detection of, I, 114  
Narceine, preparation of, VI, 400  
Pseudocodeine, VI, 395  
Sabadine, isolation of, VII, 77
- VON MERING. Composition of chondrin, VIII, 625
- MERKLEN, M. E. Detection of phenol in wood-tar creosote, III, 355
- MERL, T. Detection of colour in sausages, V, 650
- MERRYMAN. See *Silberrad*.
- MERZ, W. Starch in belladonna roots, VI, 311
- MESSINGER. Estimation of acetone, I, 100, 107
- MESSINGER. Estimation of salicylic acid, III, 481  
See *Kahrman*.
- and VORTMANN.  $\beta$ -Naphthol, estimation of, III, 258  
Phenol, estimation of, III, 301  
Phenols, estimation of, in essential oils, IX, 327  
estimation of, in thyme oil, IV, 399  
Salicylic acid, estimation of, III, 481
- MESSNER. Use of lacmoid as an indicator in the estimation of alkaloids, VI, 182, 497
- MESTREZAL. Estimation of tartaric acid in wines, IX, 106
- METT. Estimation of the proteoclastic power of pepsin, VIII, 493
- METZ. Linseed varnish, IX, 200
- METZER, K. Test for cocaine, VI, 324
- METZGES. Estimation of tannin, V, 95
- TER MEULEN. Identification of sugar present in glucosides, I, 392
- MEUNIER. Rennet-enzyme, VIII, 126
- MEUNIER, F. Estimation of asparagine, VII, 241
- MEYER. Butter fat, melting point of, II, 279  
Cottonseed oil, composition of, II, 13  
Tannins, estimation of, V, 69  
See *Harnack*, *Hersig*, *Polstorff*.  
and BRUGER. PicROTOXIDE, VII, 161



- MEYER and ECKERT.** Fatty oil and wax from raw coffee, VI, 648
- MEYER, GUSTAV.** Poisoning from potatoes, VII, 93
- MEYER, M.** Chloral yielded by chloral hydrate, estimation of, I, 272  
Coal-tar, constituents of, III, 22
- MEYER, R.** Fluorescein and ammonia, action of prolonged heating under pressure of, V, 362  
constitution of, V, 292  
Phenolphthalein, structure of, III, 550
- MEYER, R. and H.** Constitution of fluorescein, V, 292
- MEYER, V.** Nitrogen, estimation of, I, 58  
Phenylhydrazine, preparation of, VI, 31  
Vapour bath, I, 69
- MEYER, V. and C.** Determination of the vapour density of turpentine oil, IV, 408
- MEYERHEIM.** See *Marcusson*.
- MICHAEL and HIBBERT.** Nitrile structure of hydrocyanic acid, VII, 462
- MICHAELIS.** Antipyrine, formula of, VI, 37  
Proteins, coagulation of, VIII, 55  
electrocataphoresis experiments with, VIII, 89  
See *Rona*.  
and **MOSTYNSKI.** Coagulation of proteins, VIII, 55  
*RONA.* Coagulation of proteins, VIII, 55, 56  
Separation of proteins by adsorption by colloids, VIII, 57
- MICHAILOFF, W.** Detection of indoxyl-sulphuric acid in urine, VII, 256
- MICHEL.** See *Haller*.
- MICKELTHWAITE.** See *Morgan*.
- MICKO.** Meat extract, analysis of, by Bruylants' method, VIII, 420  
and bouillon cubes, IX, 615  
detection of yeast extract in, VIII, 416, 417  
estimation of xanthine bases in, VIII, 413
- MIETHE.** See *Lewis*.
- MILBAUER.** Addition of potassium persulphate in the Kjeldahl analysis of refractory substances, VIII, 49  
and **STANCK.** Estimation of pyridine in ammonia, VI, 139
- MILLAR.** Estimation of tyrosine, VIII, 87  
See *Brown*.
- MILLARD and STARK.** Pharmaceutical preparations with which antipyrine is incompatible, VI, 41
- MILLER.** Cinnamic acid, synthesis of, III, 436  
Heroin, estimation of, IX, 499  
See *Richmond*.
- MILLIAU.** Cottonseed oil, Halphen's colour test for, II, 135  
silver nitrate test for, II, 137  
Linseed oil, detection of carbon disulphide in, IX, 181  
Olive oil, detection of carbon disulphide in extracted, IX, 133  
oils, relation between iodine value for, and the melting point of their fatty acids, II, 114
- MILLIAU, BERTAINCHAUD and MALET.** Increase of acidity of olive oil, II, 110  
Suitability of olive oils for oiling wool, II, 111
- MILLIKIN.** See *Rusterholz*.
- MILLS and AKITT.** Determination of the bromine value for oils and fats, II, 27
- MUTER.** Reaction of bromine with aniline in carbon disulphide, VI, 57
- SNODGRASS.** Bromine absorption for shale oil, III, 110  
Determination of the bromine value for oils and fats, II, 26
- TAKAMINE.** Wool-keratin, VIII, 684
- MILLS, E. J.** Coal-tar, distillation of, III, 21, 23  
Colophony, densities and bromine-absorption of the distillation products of, IV, 37  
Rosin grease, formation of, IV, 46
- MILRATH.** Butyro-refractometer values for whale oil, II, 229  
Iodine value for rape oil, II, 128
- MINAJEFF.** Comparison between cotton and artificial silk, VIII, 663
- MINIATI, BOOTH and COHEN.** Separation of *o*- and *p*-toluidine, VI, 69
- MINOVICI.** Test for picrotoxin with anisaldehyde, VII, 163
- MINUNNI.** Preparation of benzoic anhydride, III, 417
- MIOLATI.** Salts of pararosaniline and crystal violet, V, 239
- MITAREWSKI.** Effect of temperature on the drying of linseed oil, II, 349  
Extraction of linseed oil from linseed, II, 325
- MITCHELL.** Glycerol in Japan wax, II, 193  
Insoluble bromide value for linseed oil, II, 29  
Use of carbon tetrachloride in the determination of the rise of temperature on the addition of sulphuric acid to fixed oils, II, 59  
See *Hekner, Winton, Wright*.
- MITCHELL, A. S.** Examination of lemon essences, IV, 357
- MITCHELL, C. AINSWORTH.** Fixed oils, fats and waxes, II, I; IX, 117  
Lard, II, 317; IX, 178  
See *W. J. Sykes*.
- MITCHERLICH.** Chemical composition of yeast, I, 208
- MITTMANN.** Composition of bay oil, IV, 315
- MOE, CARL.** Estimation of sulphide in wood pulp, IX, 84
- MÖHLAU.** Phenocyanine, V, 352  
and **ZIMMERMAN.** Estimation of indigo, IX, 428  
of indigotin, V, 402
- MOELLER, J.** Ergot in flour, VII, 23  
Ipecacuanha, VII, 49
- MOELLER, W.** Detection of sulphite-cellulose in leather, IX, 414  
Quebracho, analysis of, IX, 398  
tans in, IX, 398
- MOERCK, F. X.** Estimation of phenol, III, 300
- MOERCK.** Assay of essence of vanilla, III, 522

- MÖRNER.** Amino-acids formed by the hydrolysis of egg albumin, VIII, 20  
of serum albumin and serum globulin, VIII, 20  
Chondroproteins, VIII, 91  
 $\alpha$ - and  $\beta$ -Crystallins, VIII, 91  
Gelatin, VIII, 91  
Homogentisic acid, IX, 569  
Mucin from urine, VIII, 92  
Sugar content of eggs, IX, 620  
and FRISTEDT. Commercial asafoetida, IV, 93  
**MÖRNER, K. A. N.** Preparation of hæmin, VIII, 547  
**MOERRS.** Use of Jena-glass tubes in the Kjeldahl estimation of nitrogen, I, 61  
**MÜSLINGER.** Estimation of lactic acid, VII, 438  
See *Halenke*.  
**MOHLER.** Estimation of higher alcohols in potable spirits, I, 192  
Schiff's reagent, IX, 2  
**MOHLER, E.** Detection of benzoic acid in foods, III, 410  
**MOHR.** Ferricyanides, estimation of, VII, 528  
Keratoids, composition of, VIII, 674  
Sugar solutions, specific gravity of, I, 293  
**MOISSAN.** Opium smoke, VI, 433  
and **LANGRIN.** Aricine, VI, 547  
**MOLDENHAUER and LEYBOLD.** Estimation of ferrocyanides, VII, 512  
**MOLMAN and SONCINI.** Ozone absorption of linseed oil, II, 339  
**MONDSCHIEIN.**  $\beta$ -Hydroxybutyric acid, estimation of, IX, 578  
Lactic acid, estimation of, IX, 582  
**MONFERRINO.** Distinctive tests for antipyrine, pyramidone and nevraltine, VI, 48  
**MONIER.** Average composition of the ash of raw cane and beet sugars, I, 348  
**MONIER-WILLIAMS.** Detection of fluorides in butter and cream, VIII, 690  
**MONIN.** Estimation of lactic anhydride in commercial lactic acid, VII, 441  
**MONNET.** Detection of pseudo-tannins, IX, 409  
**MONTANARI.** Detection of salicylic acid, III, 479  
**MONTHULÉ.** Separation of caffeine and theobromine by the formation of silver theobromine, VI, 593  
**MOOR.** Porpoise oils, II, 231  
See *Allen, Chattaway, Martin, Permain*.  
and **PRIEST.** Analyses of coffee extracts, VI, 679  
**MOORE.** Carotin, detection of, in butter, v, 663  
Gelsamine, formula for, VII, 32  
isolation of, VII, 32  
Jalap, percentage of resin in, VII, 131  
Reichert value for fats and oils, II, 23  
Scopoletin, VII, 34  
See *Power*.  
and **PARKER.** Determination of the molecular weight of proteins, VIII, 77  
**ROAF.** Determination of the molecular weight of proteins, VIII, 77  
**WHITLEY.** Guaiacum test for oxydases, VIII, 13  
**MOORE, B.** Reaction of blood, VIII, 498  
**MOORE, R. W.** Asafoetida, IV, 94  
**MOORE, T. W.** Coating for coffee, VI, 670  
**MOOSER, W.** Detection of ricin in cattle foods, VIII, 110  
**MORAHT.** See *Kruss*.  
**MORAWSKI.** See *Demski*.  
and **STINGL.** Soja-bean oil, II, 146  
**MORAWSKI, T.** Test for rosin oil, IV, 43  
**MOREL, JULIUS.** Turpentine and balsams, IV, 75  
See *Hugonnet*.  
**MORELL.** Saturated acids of linseed oil, IX, 185  
**MORELL, A.** Detection of cod oil in linseed oil, II, 340  
**MORGAN and MICKELTHWAITE.**  $\alpha\alpha$ -Dicamphorarsinic acid, IV, 208  
**MORGEN.** See *Behrend, Fleischmann, Märcker*.  
**MORGENROTH.** Change of casein to paracasein, VIII, 127  
**VON MORGENSTEIN.** Quantitative separation of solanine from potato tubers, VII, 89  
Solanine in potatoes, VII, 93  
**MORIARI and SCOCCIANI.** Roasting of coffee, VI, 648  
**MORITZ and MORRIS.** Determination of the original gravity of beer, I, 154  
**MOROCHOWETZ.** Composition of chondrin, VIII, 625  
**MORPURGO.** Differentiation between boiled and unboiled linseed oils, II, 357  
**MORPURGO, G.** Detection of dulcine in wine and beer, VII, 303  
**MORRIS.** Estimation of invert sugar and saccharose, in brewing, IX, 9  
See *Brown, Moritz*.  
**MORRIS, D.** Results of analysis of india rubber by the Schneider method, IV, 114  
**MORRIS, G. H.** Rosin spirit, IV, 38  
**MORROW.** See *Bainbridge*.  
**MORTON.** See *Pennock*.  
**MORTON, H.** Absorption spectrum of alizarin, v, 213  
**MOSCHELES and STELZER.** Analyses of coffee substitutes, VI, 676  
**MOSENTHAL.** Microscopic examination of guncotton, III, 568  
Specific gravity of nitrocellulose, III, 560  
**MOSS.** Ammoniacum, IV, 91  
**MOSSLER.** Morphine in opium poppy, IX, 504  
**MOSSLER, G.** Aloes, detection of in drugs containing hydroxy-methylantraquinones, IX, 549  
**MOSTYNSKI.** See *Michaelis*.  
**MOTT, F. P.** Cider vinegar, IX, 94  
**MOUCHEL-LA-FOSSE.** See *Bongault*.  
**MOULIN.** Pyramidone, test for, IX, 471  
**MOULIN, A.** Estimation of vanillin in vanilla, III, 519  
**MOULLADE, A.** Estimation of tannin, v, 92  
**MOUREU and VALEUR.** Sparteine, boiling point of, VI, 232  
constitution of, VII, 69; IX, 483  
**MOURGUES.** Parsley oil, IV, 369  
See *Gantire*.  
**MUGGENTHALER.** See *Eibner*.  
**MÜHLHÄUSER, O.** Manufacture of orange azo-dyes, v, 137

**MÜLDER.** Chondrin, composition of, VIII, 625  
 Drying of linseed oil, II, 344  
 Gelatin, action of chlorine on, VIII, 591  
 Keratoids, VIII, 673  
 Yeast, nitrogenous constituents of, I, 208  
**MUELLER, A.** Sulphur dioxide in food gelatin, VIII, 617  
**MÜLLER.** Alkaloids, function of, in plants, IX, 478  
 Cellulose, estimation of, in wood and vegetable fibres, I, 435  
 Elastin, analysis of, VIII, 631  
 Indigotin, estimation of, by means of sodium hydrosulphite, V, 399  
 Lactic acid, separation of, from other organic acids, VII, 436  
 Morphine, solubility of, VI, 374  
 Santene in sandalwood oil, IV, 394  
 Weighted silks, analysis of, VIII, 660  
*See Albrecht, Bondi, Lampart, Lehmann.*  
 and **HAGEN.** Determination of dextrose in urine by Knapp's mercurial solution, I, 396  
**MÜLLER, A.** Analysis of the bases in crude methylamine, VI, 14  
 Separation of amines, VI, 7  
**MÜLLER, C.** Estimation of sugars, IX, 23  
**MÜLLER, F.** Detection of aniline in urine, VI, 58  
 Estimation of hæmoglobin, VIII, 561  
 Mucin from trachea and sputum, VIII, 92  
**MÜLLER, K.** Estimation of chloral yielded by chloral hydrate, I, 271  
**MÜLLER, R.** Ouabain, VII, 123  
**MULLER.** Carbonyl-ferrocyanides, VII, 532  
**MULLER, E. and SEIDEL, F.** Hydroferricyanic acid, estimation of, IX, 588  
**MULLIKEN.**  $\beta$ -Naphthol test for acetaldehyde, I, 266  
 for formaldehyde, I, 257  
 Organic acids, colour reactions of, with resorcinol, I, 487  
 and **SCUDDER.** Separation of formaldehyde and acetaldehyde, I, 264  
**MUMMERY, W. R.** *See F. T. Harry.*  
**MUNSON.** Estimation of metals in canned foods, VIII, 342  
*See Bigelow, Tolman.*  
 and **WALKER.** Estimation of reducing sugars gravimetrically, IX, 28  
 Examination of sugar products, I, 335  
**MUNSON, L. S.** Examination of inks, V, 675  
**MURAYAMA.** Japanese peppermint oil, IX, 370  
**MURDFELD.** *See Lendrich.*  
**MURLIN, J. R.** Effect of gelatin on the body, VIII, 593  
*See S. R. Benedict.*  
**MURRAY.** Estimation of caffeine, IX, 526  
**MUSPRATT.** Specific gravity of malt solutions, I, 289  
**MUSSET.** Ergot in flour, VII, 23  
 Tannin, estimation of, V, 92  
 from oak-bark, V, 26  
**MUSSO.** Analysis of Gorgonzola cheese, VIII, 251  
**MUTER.** Microscopic identification of starches, I, 411

**MUTER.** *See Mills.*  
 and **DEKONINGH.** Iodine numbers of fats and their fatty acids, II, 392  
 Separation of fatty acids by the formation of lead salts, II, 390  
**MUTER, J.** Asafoetida, IV, 93  
 Copaiba balsam, determination of fatty oils in, IV, 90  
 Quinine, estimation of, in cinchona bark, VI, 490  
**MYERS.** *See Benedict.*  
**MYLIUS and FÖRSTER.** Iodeosin as an indicator, III, 556

## N

**NÄGELI and LOEW.** Fat content of yeast, I, 208  
 Nitrogenous constituents of yeast, I, 208  
**NAEPPEN.** *See Eschweiler.*  
**NAGEL, C.** Estimation of the fermenting power of yeast, IX, 16  
**NAGELVOORT, J. B.** Distinction between gel-semine and strychnine, VII, 33  
**NALPASSE.** *See LaTour.*  
**NAPPER.** *See Robertson.*  
**NAQUET.** Hair-dye, VIII, 680  
**NASH.** Solubility of mineral oils in sperm-oil alcohols, II, 238  
**NASSE.** *See Schmitt.*  
**NASTJUKOFF, A.** Use of formaldehyde in hydrocarbon analysis, IX, 235  
**NASTVOGEL.** *See Bischoff.*  
**NATHAN.** Pure yeast culture in cider manufacture, I, 218  
 and **RINTOUL.** Manufacture of nitroglycerin, III, 570  
**NAUCKHOFF.** Freezing-point of nitroglycerin, III, 570  
**NAUDIN.** Anthemene in chamomile oil, IV, 328  
 Terpenes in angelica oil, IV, 310  
**NAUMANN and WILL.** Tannin in yeast, I, 209  
**NAUSS.** Estimation of cyanogen in spent gas purifying mass, VII, 520  
**NAWRATIL.** Assay of crude petroleum, III, 50  
**NAYLOR.** Assay of belladonna and its preparations, VI, 316  
**DE NEGRI.** Candle nut-oil, II, 149  
 Mixed fatty acids from wheat oil, II, 148  
 and **FABRIS.** Almond oil, iodine value of mixed fatty acids from, II, 103  
 Arachis oil, percentage of arachidic acid isolated from, III, 96, 97  
 Cacao butter, iodine value for the mixed fatty acids from, II, 178  
 Coffee, specific gravity of the fat in, VI, 648  
 Grape seed oil, II, 175  
 Hempseed oil, Maumené test for, II, 151  
 Linseed oil, melting-point of the fatty acids from, II, 350  
 Mafura tallow, composition of, II, 182  
 Olive oil, saponification value for, II, 115  
 Soja-bean oil, solidifying of, II, 146  
**NELSON.** Constituents of spearmint oil, IX, 372  
**NELSON, E. K.** Ascaridol, IX, 382

- NENCKI and SIEBER.** Preparation of hæmin, VIII, 546
- ZALESKI.** Hæmatoporphyrin and its derivatives, preparation of, VIII, 552, 553  
Hæmin, ethers and esters of, VIII, 548  
preparation of, VIII, 548  
Hæmopyrrole, VIII, 558  
Mesoporphyrin, VIII, 555
- NEOGI.** Coniinium nitrate, IX, 481
- NERKING and HAENSEL.** Estimation of lecithin in milk, VIII, 162
- NESSLER and BARTH.** Estimation of tannin in wines, I, 175  
Rate of evaporation of glycerol, II, 456
- NESTLER.** Testing of saffron, V, 420
- NESTLER, A.** Detection of coffee in extracts, VI, 646
- NEUBAUER.** Gallotannic acid, reduction equivalent of, V, 64  
Oak-bark tannin, reduction equivalent of, V, 64  
Tannin, estimation of, in wines, I, 175  
Urine, occurrence of hæmatoporphyrin in, VIII, 555
- NEUBERG.** Glycuronic acid, formation of, from purrée, VII, 396  
Lactic acid, tests for, IX, 582  
Lævulose methyl-phenyl-osazone, I, 375  
See *Albu, Lowy, Mandel.*  
and **KARCZAG.** Isobutylamine as a putrefaction product, VII, 345  
**MARX.** Detection of raffinose in the presence of sucrose, I, 314  
**NEIMANN.** Estimation of glycuronic acid in urine, VII, 399
- NEUMANN.** Hops, estimation of resins in, IX, 554, 557  
Nucleic acid, isolation of, VIII, 71  
Proteins, estimation of phosphorus in, VIII, 80  
See *Bauer, Kreidl, Parow, Tappeiner.*
- NEVILLE.** Mucilage in linseed, IX, 182
- NEW YORK TESTING LABORATORY.** Float apparatus for determining viscosity, III, 105
- NEWHALL.** See *Woodman.*
- NEWMAN.** Phenosafranine, V, 322  
See *Norton.*
- NICHOLAS.** Distinction between boiled and un-boiled milk, VIII, 15
- NICKELS.** Specific gravity of benzene, III, 203
- NICKELS, B.** Aniline oils, test for, VI, 79  
Benzol, commercial, assay of, III, 234  
distillation of, in the presence of carbon disulphide and light hydrocarbons, III, 237, 238  
Carbon disulphide, effect of the elimination of, on the density of benzol, III, 228  
estimation of, in commercial benzols and naphthas, III, 226  
Coal-tar naphtha, crude, fractional distillation of, III, 221  
Gas-works tar, assay of, III, 25, 26  
Naphthas, comparative results of the distillation of, by the retort method and the bulb-tube method, III, 236  
Phenyl-naphthylimide, detection of, in crude anthracene, III, 282
- NICLOUX.** Detection of carbon monoxide in blood, VIII, 535  
See also *Desgrez.*
- NICOL, C.** Estimation of anthracene in coal-tar, III, 285
- NICOLAIE and DOHRN.** Atophan, effect of ingestion of, IX, 570
- NICOLS.** Specific gravity of aqueous solutions of glycerol, II, 448
- NIEBEL, W.** Detection of horse flesh in sausages, VIII, 378  
Percentage of glycogen in flesh, VIII, 282  
and **SALKOWSKY.** Estimation of glycogen in flesh, VIII, 282
- NIEDERHOFHEIM.** See *Fraud.*
- NIEGEMAN.** Linseed oil, unsaponifiable matter in, II, 333  
use of, for varnish, etc., II, 328
- NIEMANN.** See *Neuberg.*
- NIERENSTEIN.** Cheese, nature of the fat in, VIII, 246  
Ellagic acid, V, 23, 24  
 $\beta$ -Guaranine, VI, 683  
Tannin, constitution of, IX, 385  
estimation of, V, 87  
formula for, V, 17  
and **RIXON.** Leucoellagic acid, IX, 385  
**WEBSTER.** Sumach, adulteration of, V, 102  
estimation of catechol tannins in, V, 8
- NIETZKI.** Classification of sulphur dyes, V, 375  
Molecular formula of nigraniline, V, 312  
and **SCHROETER.** Fluorescein, V, 287  
and fluorap, salts of, V, 291
- NIOBEY.** See *Conty.*
- NIPPE.** Preparation of hæmochromogen, VIII, 549
- NITSCHER.** Melting point of glycerol, II, 447
- NOEL.** See *Le Bon.*
- NOELTING.** Composition of the volatile phenols of creosote oil, III, 366
- NÖLTING and BOASSON.** Estimation of aniline and methyl-aniline, VI, 92  
and **PICK.** Wroblewsky's. o-xyloidine, VI, 71
- NÖRDLINGER.** o-Cresol, III, 313
- NÖTEL.** Testing for horse flesh, VIII, 273
- DI NOLA.** See *Bianchi.*
- NOLTNER.** Change of colour of potassium thiocyanate when heated, VII, 546
- NORDLINGER.** Composition of palm oil, II, 183  
and **THOMSON.** Free fatty acids in linseed oil, II, 333
- NORLIN.** See *Klason.*
- NORMAN and HUGEL.** Hydrogenation of castor oil, IX, 124  
See *Tauber.*
- NORMANN.** Polymerisation of tung oil, II, 155
- NORRIS.** See *Harden.*  
and **SANDERS.** Formation of triphenylcarbinol from triphenylmethyl chloride, V, 238
- NORTHALL-LAURIE, D.** Estimation of toluene in toluol, IX, 230
- NORTON.** Analysis of crude gluten from durum flour, VIII, 99  
and **NEWMAN.** Reaction of hydrastine, VI, 568

- NOTENAGEL, G. Artificial muscarine, VII, 285  
 NOTTBOHM. See *Lendrick*.  
 NOVY. Propyl and iso-butyl esters of cocaine, VI, 328  
 NOVY, E. C. Detection of poisonous meat by feeding experiments, VIII, 326  
 NOWAK. Estimation of sugars, IX, 56  
 NUNN, A. W. Estimation of camphor in camphor liniment, IV, 199  
 NUTTALL. Precipitin test for blood, VIII, 577

## O

- OBACH, E. F. A. Gutta-percha and balata, commercial, composition of, IV, 158  
 extraction and purification of, IV, 156  
 OBERFELL. Chroming of hide powder, V, 82  
 OBERFELL, C. R. Analysis of leather, IX, 414  
 OBERLÄNDER. See *Tschirch*.  
 OBERMAYER. Estimation of coumarin, IX, 294  
 OBERMILLER. Phenol sulphonic acids, III, 393, 394, 395  
 estimation of, III, 397  
 OBOLENSKY. Analysis of mucin, VIII, 628  
 OBOLONSKI. Identification of colchicum, VII, 12  
 ODDO and COLOMBANO. Alkaloid from solanum sodomæum, VII, 89  
 OERUM. Estimation of dextrose with Sachse's mercuric solution, I, 338  
 OESTERLE. Bornträger's test for aloes, VII, 144  
 Chrysarobin, V, 228  
 See *Tschirch*.  
 and JOHANN. Chrysophanic acid, V, 227  
 OFFENHAUR. See *Stohmann*.  
 OFFERDAHL-LARVIK. Nickel in hardened oils, IX, 125  
 OGDEN. Percentage of sucrose in maple products, I, 388  
 See *Winton*.  
 OGILVIE. Estimation of saccharose, IX, 45, 46  
 OGLIALORO. See *Palernò*.  
 OGLOBINI. See *Markownikoff*.  
 OGSTON. See *Way*.  
 OKUDA. Nitrogen of fish muscle, IX, 621  
 OLIG and TILLNANS. Mean molecular weights of soluble and insoluble fatty acids from butter, II, 287  
 OLIVER. Hæmoglobinometer, VIII, 564  
 Morphine, detection of, IX, 498  
 OLIVERI. Achis oil, Ar iodine alues fr, 920AII  
 Olive oil, oleo-refractometer tests for, II, 116  
 saponification value for, II, 115  
 OLSEN and RATNER. Drying of linseed oil, IX, 199  
 OLSON. Estimation of proteins in milk, VIII, 155  
 Milk protein from separator slime, VIII, 140, 184  
 OLTOLENGHI. Decomposition of meat, IX, 612  
 OPPENHEIMER. Lactic acid, estimation of, IX, 583  
 ORDONNEAU. Estimation of tartaric acid, IX, 104  
 ORLOFF. Analysis of Russian koumiss, VIII, 231  
 ORNDORFF and BREWER. Constitution of coerulein, V, 299  
 CAMERON. Dianthrane, III, 263  
 ORTHMANN. See *Levi*.  
 ORTON. Composition of rock-asphalt, III, 61  
 See *Edwards*.  
 EDWARDS and KING. Purification of acetic acid, IX, 90  
 and GARROD. Detection of homogentisic acid, VII, 405  
 OSBORNE. Edestin, VIII, 109  
 Legumelin, VIII, 111  
 Potatoes, protein of, VIII, 96  
 Soy bean, proteins of, VIII, 112  
 Vicilin, VIII, 111  
 See *Carr*.  
 and CAMPBELL. Amandin, VIII, 109  
 Conalbumin, VIII, 91  
 Conglutins of yellow lupins, VIII, 112  
 Egg-white, proteins of, VIII, 433  
 Globulins, VIII, 91  
 Proteins of barley, change in, on germination, VIII, 104  
 CLAPP. Amandin, VIII, 109  
 Dipeptide, VIII, 471  
 Nordein, hydrolysis of, VIII, 104  
 Pea legumin, hydrolysis products of, VIII, 111  
 Phaseolin, hydrolysis products of, VIII, 112  
 Prolamin in rye and gliadin, VIII, 108  
 Zein, hydrolysis products of, VIII, 107  
 GUEST. Hydrolysis products of casein, VIII, 120  
 HARRIS. Amandin, VIII, 109  
 Edestin, solubility of, in inorganic salt solutions, VIII, 109  
 Hausmann numbers of proteins, determination of the, VIII, 81  
 Nitrogen in hordein, VIII, 104  
 Plant proteins, optical rotation of, VIII, 77  
 precipitation of, by ammonium sulphate, VIII, 77  
 HEYL. Hydrolysis products of vetch legumin, VIII, 111  
 LEAVENSWORTH and BRAUTLECHT. Separation of diamino-acids formed by protein hydrolysis, VIII, 28, 32  
 MENDEL and HARRIS. Ricin, VIII, 110  
 and VOORHEES. Wheat proteins, VIII, 96  
 OSBORNE, T. B. and JONES, B. Amino-acids, esterification of, IX, 562  
 Protein hydrolysis, examination of the products of, VIII, 28  
 plant, VIII, 95  
 separation of mono-amino-acids formed by, VIII, 22  
 OSER. Reduction equivalent of oak-bark tannin, V, 64  
 OSSWALD. See *Hantzsch*.  
 OST. Solubility of salicylic acid, III, 466  
 OST, H. Detection of pyridine in commercial ammonia, VI, 137  
 and KLEIN, F. Estimation of formic acid in acetic acid, I, 494  
 OSTERBERG. See *Wolf*.  
 OSTERMEYER. Estimation of tannins, V, 90  
 O'SULLIVAN. Carbohydrates, hydrolysis of, I, 297  
 Gums, composition of, I, 439

- O'SULLIVAN. Starch, estimation of, by the diastase method, I, 420  
 Sugar, reducing, estimation of, IX, 24  
 solutions, specific gravity of, I, 289  
 and TOMPSON. Effect of acid on the measurement of the activity of invertase, VIII, 8  
 OSWALD. Thyreoglobulin, VIII, 92  
 OTTO. Terpenes, IV, 166  
 Use of mercuric solutions in the estimation of dextrose, I, 337  
 See *Wallach*.  
 OTTOLENGHI. Ergosterol, II, 488  
 OUDEMANN. Alcohol, estimation of, in commercial chloroform, I, 278  
 Conquinamine, VI, 537  
 Palm-nut oil, composition of, II, 195  
 Podocarpic acid, IV, 5  
 Quinine sulphate, optical assay of, VI, 524  
 OUTERBRIDGE. Detection of mineral oil in linseed oil, IX, 195  
 OUTON. Analysis of commercial acetylene, III, 9  
 OVERBECK. Preparation of nitroprussic acid, VII, 530  
 OWEN, F. A. Estimation of indigotin, V, 402
- P
- PAAL and ROTH. Reduction of oleic acid by colloidal platinum, II, 375  
 PAAL, C. Gelatones, VIII, 595  
 PADÉ, L. Estimation of sulphites in food gelatin, VIII, 617  
 Specific gravity of coffee berries, VI, 669  
 PAESSLER. Chestnut-oak bark, IX, 396  
 Lactic acid, estimation of, in lactates, VII, 448  
 Tan-liquors, estimation of volatile acids in, V, 99  
 Tannin extracts, non-tans and tans in, IX, 400  
 sugar content of, IX, 406  
 and HOFFMAN. Myrabolans, IX, 395  
 PAESSLER, J. and VEIT, T. Solubility of tannin extracts, V, 82  
 PAETZOLD, E. P. Adulteration of rose oil, IV, 386  
 PÄYKUL. Mucin from bile, VIII, 92  
 PAGAMINI. Detection of sawdust in flour, I, 462  
 PAGÈS. See *Arthur, Imbert*.  
 PAGLIANI. Use of salicylic acid in alkalimetry, III, 476  
 PAHL. See *Heinzerling*.  
 PAIN. Test for santonin, VII, 154  
 PAINE. See *Hudson*.  
 PAISLEY. See *Endemann*.  
 PALADINO. Coffearine, VI, 647  
 and TOSO. Egg oil, II, 203, 204  
 Egg-fat, use of, in ointments, VIII, 435  
 PALASSAY. Analysis of Virginia sumac, V, 37  
 PALKIN, S. See *W. O. Emery*.  
 PALM, R. Lactic acid, detection of, in animal or vegetable organs, VII, 433  
 estimation of, VII, 440  
 Picrotoxin, test for, VII, 162  
 DI PALMA.  $\alpha$ -Lupanine, action of heat on, IX, 482  
 PALMER. See *Richards*.  
 PANCHAUD. Assay of aconite, VI, 281  
 PANCOAST and KEBLER. Congealing point of anise oil, IV, 312  
 PANEK. See *Bondsinski*.  
 PANIKER and STIASNY. Gallotannic acid, IX, 385  
 PANTING. See *Wade*.  
 PAOLINI. Apomorphine, salts of, IX, 499  
 Thujyl alcohol, IX, 343  
 See *Balbiano*.  
 PAPE, C. Assay of opium, VI, 428  
 PARASCHTSCHUK. Analysis of Dutch cheese, VIII, 251  
 PARASTSCHUK. See *Pawlow*.  
 PARIS. Estimation of lactic acid, VII, 440  
 PARIS, G. Cocoa husks, VI, 696  
 PARKER. Non-tans, value of, in tanning, V, 83  
 Tannin solution, treatment of, with hide powder, V, 84  
 Tannins, extraction of, V, 3  
 See *Moore*.  
 and PAYNE. Berkefeld candle, V, 79  
 PARKER, GORDON. Analysis of leather, V, 105  
 PARKIN. Sugar analysis, IX, 50  
 PARMEGGIANI. Saccharin, detection of, III, 433  
 estimation of, III, 435  
 reactions of, III, 430  
 PAROW, ELLRODT and NEUMANN. Specific gravities of various starches, I, 407  
 and NEUMANN. Polarimetric estimation of starch, I, 425  
 PAROZZANI, A. See *Culpiani*.  
 PARR, S. W. Calorimeter, III, 51  
 PARRY. Amber, oil of, IV, 21  
 Aniseed oil, IX, 351, 352  
 Asafoetida, lead number of, IX, 318  
 Camphene, occurrence of, IV, 182  
 Cassia oil, adulteration of, IX, 293  
 Cinnamon oil, adulteration of, III, 444  
 Citral, estimation of, IV, 271, 276  
 Citronellal, specific gravity of, IV, 269  
 Citronella oils, test for, IV, 305  
 Clove oil, specific gravity of, IV, 330  
 Codliver oil, constants for the fatty acids from, II, 215  
 Colophony, detection of, in shellac, IV, 69;  
 IX, 312  
 Copaiba oil, adulteration of, IV, 84  
 Coriander oil, IV, 333  
 Dill oil, composition of, IV, 335  
 Essential oils, IV, 217; IX, 324, 345  
 estimation of aldehydes and ketones in, IV, 232  
 refractive index of, IV, 245  
 Eucalyptus oils, estimation of cineol in, IV, 339  
 Fatty and resin acids, separation of, IV, 73  
 Geranium oil, adulteration of, IX, 361  
 indices of refraction for, IV, 344  
 Guaiacum, IX, 311  
 Juniper oil, IV, 346, 347  
 Lemon-grass oil, IV, 308  
 Nutmeg oil, IV, 358  
 Orange oil, IV, 361, 362  
 sweet, composition of, IV, 359  
 Pepper, microscopical examination of, VII, 59  
 Resins, IX, 310



- PARRY.** Rose oil, iv, 386  
 Rosemary oil, iv, 390  
 Rosin, estimation of, in printing inks, ix, 459  
 Sandalwood oil, iv, 395  
     acetylation process for the examination of, iv, 394  
 Shellac, iv, 70  
 Terpeneless essential oils, iv, 429  
 Terpentine oil, ix, 378  
 and BENNET. Citronella oil, adulteration of, iv, 306  
     standards for, iv, 307  
 Peppermint oil, adulteration of, iv, 374, 375  
 Rosemary oil, iv, 390; ix, 374  
 Sandalwood oil, iv, 393  
 Spike-lavender oil, adulteration of, iv, 351  
**PARSONS.** Drying of sensitive organic substances, i, 68  
 and WRUMPELMEIER. Berberine phosphate, vi, 561  
**PARSONS, H. P.** Hydrated quinine sulphate, vi, 516  
**PARTHEIL.** Lactic acid, estimation of, vii, 438, 439  
     separation of, from other organic acids, vii, 436  
 and FÉRIÉ. Separation of saturated and unsaturated fatty acids by their lithium salts, ii, 392  
 VAN HAAREN. Specific rotation of camphor, iv, 194  
**PARTHEIL, A.** Isolation of cytisine, vii, 13, 15  
**PASCHKIS.** Phytosterol from colchicum seeds, ii, 485  
 and SMITA. Alkaloid from *Lobelia inflata*, vi, 224  
**PASCHKIS, H.** Fluorescent substance from belladonna berries, vi, 311  
**PASSMORE.** See *Fischer*.  
**PASTERNAK.** See *Juckenack*.  
**PASTEUR.** Culture and cleaning of yeast, i, 216  
     See *Liebig*.  
**PATERNÒ and OGLIALORO.** Picrotoxin, vii, 160  
**PATRICK.** Estimation of water in butter, ii, 306  
**PATRICK, G. E.** Gelatin, detection of, ix, 605  
**PATTEN.** See *Kossel*.  
**PATTERSON.** Absorption spectrum colorimeter for the examination of oils, ii, 42  
     Capillary speeds of aniline colours, v, 442  
**PAUL, B. H.** Cinchona barks, analysis of, vi, 484  
 Coca, amorphous base of, vi, 343  
 Cocaine benzoate, commercial, vi, 327  
     crude, vi, 328  
     hydrochloride, purity of, vi, 329, 332  
     solubility of, in water and in chloroform, vi, 321  
 Emetine, percentage of, in de-emetinised ipecacuanha, vii, 49  
 Kerner test for quinine sulphate, vi, 520, 521  
**PAUL and COWNLEY.** Cinnamyl-cocaine, vi, 340  
 Caffeine, estimation of, in tea and coffee, vi, 611  
 Cocaine, purity of, vi, 329  
 Coffee, percentage of caffeine in, vi, 656  
     roasting of, vi, 649  
**PAUL and COWNLEY.** Homoquinine, vi, 549, 550  
 Ipecacuanha alkaloids, vii, 38, 40, 48  
     isolation of, ix, 542  
 Psychotrine, ix, 544  
**PAULI.** Proteins, coagulation of, viii, 55  
     precipitation of, viii, 37  
 Tannins, estimation of, v, 60  
 and HANDOVSKY. Coagulation of proteins, viii, 55  
**PAULMANN, W.** Preparation of sarcosine by the hydrolysis of caffeine, vii, 272  
**PAULMEYER.** Composition of coconut oil, ii, 188  
**PAVESI.** Aporeine, vi, 396; ix, 501  
**PAVY.** Reducing substances in fish, viii, 460  
**PAVY, F. W.** See *Siew, R. L.*  
**PAWLEWSKI.** Petroleum from Kleczany, iii, 43  
**PAWLOW and PARASTSCHUK.** Rennet-enzyme, viii, 126, 129  
**PAYEN.** Animal foods, composition of, viii, 263  
 Caffetannic acid, vi, 645  
 Sugar-cane, analysis of, i, 359  
 Yeast cellulose, i, 209  
 and CHEVALIER. Bitter substance from hops, vii, 169  
**PAYET.** Distinction between gum arabic and gum tragacanth, i, 445  
**PAYNE.** See *Fischer, Parker, Revis*.  
**PEACHY.** See *Pope*.  
**PEANO.** Determination of the oil in olives, ii, 106  
**PEARMAN.** Table of values for oils and fats with the oleo-refractometer, ii, 44  
     See *Chattaway*.  
 and MOOR. Iodine absorption of sandalwood oil, iv, 395  
**PEARSON, W. A.** Determination of the amount of alcohol in concentrated spirit of nitrous ether, i, 247  
**PEASSLER.** Analysis of mimosa barks, v, 39  
**PECKELHARING.** Pepsin, viii, 491  
**PECKHAM.** Asphalt, comparison of analyses of, by Linton's and Sadtler's methods, iii, 89  
     composition of, iii, 57  
     Bitumens, classification of, iii, 38  
     examination of, iii, 90  
     origin of, iii, 37  
**PECKOLT, THEODORE.** Analysis of maté, vi, 642  
**PEDERSON.** See *Tschirch*.  
**PEGAMI, A.** See *M. Tortelli*.  
**PÉGURIER.** Estimation of pyramidone in presence of antipyrine, vi, 49  
     See *Astruc*.  
**PEKESCHEN, C.** Alkaloids from the Hellebores, vii, 79  
**PEINE.** Synthesis of cinnamaldehyde, iii, 441  
**PEKELHARING.** Nucleoproteins of meat and the mucous membrane of stomach, viii, 92  
**PELIGOT and BUIGNET.** Extraction of cane sugar in the presence of invert sugar, i, 341  
**PELLET.** Lævulose and dextrose, estimation of, in mixtures, i, 375  
     Saccharose, estimation of, ix, 43, 46  
     Salicylic acid, detection of, iii, 478  
     in wine, iii, 477



- PELLET.** Sugar analysis, IX, 49, 50, 51, 52  
 estimation of, in beet, I, 360  
 solutions, refractometer values of, IX, 21  
 use of basic lead acetate in clarifying, I, 311  
 Sugars, estimation of, I, 333; IX, 23  
 reducing, estimation of, IX, 25, 42  
 and **DE GROBERT.** Estimation of salicylic acid, III, 484
- PELLETAN.** See *Chevallier*.
- PENCE, C. M.** Cresols, estimation of, IX, 272
- PENNINGTON.** Analyses of chicken, VIII, 431  
 Frozen eggs, VIII, 449  
 See *Wiley*.  
 and **GREENLEE.** Estimation of preformed ammonia in flesh, VIII, 316
- HEPBURN.** Estimation of free fatty acids in meat fat, VIII, 318
- ROBERTSON.** Effect of cold storage on the enzymes in eggs, VIII, 445
- PENNOCK and MORTON.** Estimation of pyridine in ammonia, VI, 138
- PERCIABOSCO.** See *Cansoneri*.
- PERCIVAL.** Morphology of hops, VII, 171
- PEREIRA.** Detection of salicylic acid in wine, III, 477
- PERGAMI.** See *Tortelli*.
- PERKIN.** Alizarin, v, 208  
 paste, analysis of, v, 217  
 Cinnamic acid, synthesis of, III, 436  
 Coumarin, synthesis of, III, 447  
 Hydriodic acid, action of, on alkaloids, VI, 203  
 Indoxyl brown, v, 385  
 Tannin, constitution of, v, 19  
 Terpinolene, synthesis of, IV, 171  
 See *Dobson, Frank, Green*.  
 and **ROBINSON.** Constitution of harmine and harmaline, VII, 36  
 Identity of racemic narcotine and gnoscopine, VI, 397
- PERKIN, A. G.** Berberine, VI, 552  
 Cape sumac, colouring principle of, v, 55  
 Indigo yellow, v, 389  
 See *W. P. Bloxam*.  
 and **BLOXAM, W. P.** Indigo brown, v, 389  
 Preparation of indican, v, 384
- PERKIN, W. H.** Anthracene and its associates, behaviour of, with solvents, III, 274  
 Berberine, formula of, v, 360  
 oxidation of, VI, 554  
 Essential oils, determination of the methoxyl numbers of, IV, 240
- PERKIN, W. H., JR.** Constitution of berberine, VI, 552  
 Synthesis of dipentene, IV, 173
- PERRIER.** Chrysanthemum oil, IV, 329
- PERRINS.** Berberine, VI, 552
- PERROT and GORIS.** Colophony, detection of, in balsam, III, 461  
 Kolanin, composition of, VI, 682  
 Tea flowers, dried, VI, 601
- PERRY, F.** See *B. F. Howard*.
- PERSONNE.** Commercial chloroform, I, 276
- PERSOZ.** Estimation of weighting in silk, VIII, 656
- PERTUSI.** See *Camilla*.
- PERTUSI, C. and GASTALDI, E.** Hydrocyanic acid and cyanides, detection of, IX, 585
- PETER.** Action of oils on polarised light, II, 45
- PETERMANN, A.** Analyses of chicory, VI, 674
- PETERS.** Ethyl alcohol, estimation of, in fusel oil, I, 131  
 Oxygen capacity in hæmoglobin, VIII, 522  
 Rennet coagulation, compounds which retard, VIII, 130  
 Sugars, estimation of, IX, 57  
 See *Wilkinson*.
- PETERSEN.** Estimation of hydrazine, VI, 26  
 Snake-root oils, IV, 397
- PETIT.** Ammonia test for eserine, VII, 25  
 Extraction of linseed oil from linseed, II, 326  
 and **POLONOVSKY.** Artificial tropeines, VI, 301  
 Melting point of eserine, VII, 24  
 Pilocarpine and its salts, VII, 51
- TERRAT.** Estimation of caffeine in tea, VI, 610
- PETIT, A. and A.** Assay of opium, VI, 426
- PETITT.** Boiling point of methyl alcohol, I, 86
- PETKOW.** Constants for walnut oil, II, 158  
 Silver nitrate test for cottonseed oil, II, 136
- PETRIE.** Glucosides, cyanogenetic, IX, 545  
 Mydriatic alkaloid in *Solandra lævis*, VI, 290
- PFÄFF.** Specific gravity of mastic, IV, 59
- PFEIFFER.** Formation of cyanogen compounds in the manufacture of coal gas, VII, 456  
 See *Einhorn*.
- PFEIFFER, H. T.** Manufacture of crude cocaine hydrochloride from coca leaves, VI, 348
- PFISTER, A.** Colour reactions of opium alkaloids, VI, 368
- PFLEGER.** Manufacture of sodium cyanamide, VII, 557  
 Preparation of potassium cyanide, VII, 475
- PFLEIDER.** Action of acids on coagulation by rennet, VIII, 129
- PFLÜGER.** Estimation of glycogen in flesh, VIII, 284
- PHELPS and TELLOTSON.** Separation of mono-amino-acids formed by the hydrolysis of proteins, VIII, 22
- PHILIPP.** See *Foersterling*.
- PHILIPP, HERBERT.** Cyanogen and its derivatives, VII, 453; IX, 585
- PHILIPPE.** Detection of salicylic acid, IX, 301  
 Extraction of benzoic acid from milk, IX, 281
- PHILIPS.** Hydrastine, VI, 564
- PHILLIPS, F. C.** Nitrogen in natural gas from Pennsylvania petroleum, III, 41
- PIAZZA.** See *Tortelli*.
- PICCININI.** Pseudo-pelletierine, VI, 231
- PICK.** Protein digestion products, VIII, 473  
 See *Nöbling*.
- PICKARD, LEWCOCK and YATES.** Fenchyl alcohol, IX, 343  
 LITTLEBURY. Isomenthol, IX, 343  
 Neo-menthol in peppermint oil, IX, 370
- PICKLES.** Distillation of rubber, IV, 109  
 Hydrocarbon in india-rubber, IV, 108  
 and **WHITEFIELD.** L-Methylinositol in raw Para rubber, IX, 320

- PICTET.** Formation of alkaloids in plants, vi, 169  
 Synthesis of nicotine, vi, 237  
 and **ATHANASESCU.** Constitution of laudanone, vi, 361  
**COURT.** Volatile alkaloids, vi, 236  
 base of pepper, vii, 56  
**GAMS.** Berberine, synthesis of, ix, 521  
**KRAMERS.** Colour reaction of opium bases with sulphuric acid, vi, 367  
 Colour reactions of papaverine, vi, 403  
**PIERAERTS, J.** Lævulose, action of, on orcinol, i, 401  
 reducing power of, i, 374  
**PILHASHY, B. M.** Dimethylaniline test for formaldehyde, i, 259  
**PILKINGTON, B.** See *H. V. Tartar*.  
**PILLSBURY, B.** Poisoning by methyl salicylate, iii, 493  
**PILOTY.** See *Fischer*.  
 and **DORMANN.** Hæmopyrrole, viii, 559  
**STOCK.** Constituents of hæmopyrrole, viii, 558  
**THANNHAUSER.** Hæmopyrrole, viii, 559  
**PILOTY, O.** Hæmatin, conversion of, to hæmin, viii, 548  
 Hæmopyrrole, viii, 559  
**PINETTE.** Linoleum, ii, 362  
 Specific gravity and coefficients of expansion of the cresols, iii, 312  
**PINKUS.** See *Hopkins*.  
**PINNER.** Constitution of pilocarpine, vii, 52  
 and **SCHWARZ.** Constitution of iso-pilocarpine, vii, 53  
 Pilocarpine, vii, 51  
**PINTUS, A. SANNA.** Detection of abrastol in wines, iii, 402  
**PIRIA.** Preparation of benzaldehyde, iii, 417  
 of salicylic acid, iii, 466  
**PIUTTI and BENTIVOGLIO.** Detection of colouring matters in food, v, 653  
**PIVERLING.** Carnaúba wax, ii, 270  
**PLAHL.** Detection of bilberry juice in red wine, v, 655  
**DE PLATO.** Tobacco seed, alkaloids in, ix, 477  
**PLATTNER.** See *Jensen*.  
**PLENGE, H. C.** Preparation of aloin from aloes, vii, 141  
**PLIMMER, R. H. ADERS.** Arginine, ix, 625  
 Cystine and tyrosine, separation of, viii, 689; ix, 563  
 Livettin, viii, 92  
 and **BAYLISS.** Proteins, estimation of phosphorus in, viii, 80  
 and **SCOTT.** Distinction between nucleoproteins and phosphoproteins, viii, 71  
**SCOTT.** Phosphoprotein in the pancreas, viii, 74  
**SKELTON.** Urea, estimation of, ix, 564  
**PLIMPTON and GROVES.** Estimation of halogens in volatile organic substances, i, 63  
**PLLÜGER.** Extraction of fat from animal tissues, ix, 223  
**PLUGGE.** Ammoniacum, iv, 91  
**PLUGGE.** Opium alkaloids, separation and estimation of, vi, 370  
 bases, test for, vi, 366  
**PODA.** Pumpkin seed oil, ii, 70, 141  
**POETSCHKE.** Estimation of borax in soap, ix, 208  
**PÖHL.** Constitution of spermine, vii, 203  
 Globulins, viii, 91  
**PORTOLET.** Sandalwood oil, iv, 395  
**POLASEK.** See *Tschérck*.  
**POLECK and WEBER.** Composition of the ash of white of egg, viii, 422  
**POLENSKE.** Benzoic acid, detection of, ix, 280  
 estimation of, ix, 284  
 Butter fat, values for, ix, 152, 153  
 Coconut oil in butter fat, ii, 296  
 Lard, determination of water in, ii, 320  
 Phytosterol, effect of feeding animals with, ii, 489  
**POLENSKE, E.** Sweet-pickle cure for meat, viii, 355  
**POLLAK, J.** See *E. Lippmann*.  
**POLONOVSKY.** See *Petit*.  
**POLONY, C. J.** Reclaiming of soft vulcanised rubber, iv, 153  
**POLONYI, H.** See *F. Epstein*.  
**POLOTZKY.** See *Herszog*.  
**POLSTORFF.** Betaine in kola nuts, vi, 683  
 Choline in tea leaves, vi, 599  
 Pseudomorphine, constitution of, vi, 357  
 Trigonelline in coffee, vi, 648  
 and **MEYER.** Cyanides, estimation of halogens in, ix, 587  
**POMMERHNE.** Berberine, vi, 552  
 Melting point of oxyacanthine, vi, 562  
**PONTIO.** Vulcanised rubber, analysis of, iv, 132  
 extraction of, iv, 128  
 Sulphur, estimation of, in india rubber, iv, 126  
**PONZIO.** Arachidic acid in rape oil, ii, 123  
**POOL.** Detection of oil of cloves in oil of cinnamon, iii, 445  
**POPE.** Japaconitine, vi, 266  
 Sulphonation of camphor, iv, 203  
 See *Baker, Ling*.  
 and **HARVEY.** Resolution of asymmetric tetraalkylammonium compounds into active components, vi, 23  
**PEACHY.** Resolution of asymmetric tetraalkylammonium compounds into active components, vi, 23  
**POPE, F. G. and HOWARD, H.** Formula for fluorones, v, 290  
**POPESCU.** Detection of chicory colour in white wines, v, 655  
**POPP.** See *C. Fresenius*.  
**PORTÈLE, K.** Factitious coffee-beans, vi, 664  
**PORTES and DESMOULIÈRES.** Occurrence of salicylic acid in strawberries, iii, 466  
**LANGLOIS.** Assay of opium, vi, 423, 424  
**PORTMANN, G.** Detection of minute traces of hydrocyanic acid, vii, 469  
**PORUMBARU.** Formation of sugar from gelose, viii, 622  
**POSETTO.** Substitute for cacao butter, ii, 179

- POSSETTO and ISSOGLIO. Estimation of saccharin, IX, 290
- POST. Phenol sulphonic acids, III, 393
- POTOLIET. Acetylation process for the examination of sandalwood oil, IV, 394
- POTONIC. See *Helm*.
- POTTER. See *Jowell, Umney*.
- POUCHAND. Estimation of cinnamic aldehyde, III, 441
- POUTET. Elaidin reaction for fixed oils, II, 39
- POWELL, J. R. Soaps, IX, 204
- POWER. See *Salway*.  
and KLEBER. Bay oil, composition of, IV, 315  
Oil of sweet birch, composition of, III, 494  
of wintergreen, composition of, III, 493  
Peppermint oil, American, IV, 370  
estimation of menthol in, IV, 229
- LEES. Bay oil, IX, 352  
Methyl-*n*-heptyl ketone, IV, 190  
Methyl-nonyl ketone, IV, 189  
Snake-root oils, IV, 397
- MOORE. Colocynthin and colocynthein, VII, 158
- SALWAY. *n*-Methylcytisine, IX, 535  
Myristian, IX, 383  
Nutmeg oil, IV, 358  
Phytosterolins, IX, 545  
Sarsaparilla root, IX, 548
- POWER, F. B. Bismuth salicylate, assay of, III, 491  
Hydrastine, specific rotation of, VI, 566  
Peach kernel oil, nitric acid test for, II, 105  
Salicylic acid, estimation of, III, 482  
Snake-root oils, IV, 397
- and ROGERSON. Mexican scammony root, VII, 133
- TUTIN. Glycerolphosphoric acid, II, 452  
Oleasterol, olestranol and homo-olestranol, II, 488  
Phytosterol from eriodictyon californicum, II, 486
- and ROGERSON, H. Hops, constituents of, IX, 550  
valuation of, IX, 556
- POWICK. See *Chapin*.
- POWNEY. Drying of linseed oil, IX, 192
- PRATT. See *Hampshire*.
- PRATT, D. S. Fruit, estimation of citric acid in, IX, 113  
of malic acid in, IX, 98
- PREGI. Decomposition of carboxyhæmochromogen to hæmatin, VIII, 552  
See *Abderhalden*.
- PRESCOTT. See *Ewell, Hess, Knox*.
- PRESCOTT, A. B. Black and green teas, preparation of, VI, 597  
Cinchonine, solubility of, VI, 541  
Mayer's reagent for alkaloids, VI, 191, 192  
Morphine, solubility of, VI, 375  
Opium, assay of, VI, 423  
Tannins, classification of, V, 5  
Vegetable substances, analysis of, I, 445  
See *Gordin*.
- and GORDIN. Aconite, assay of, VI, 279  
Opium, assay of, VI, 428
- PRESCOTT and GORDIN. Periodides of the alkaloids, VI, 190  
Strychnine, estimation of, in hypodermic tablets, VI, 463
- PRESSE and STANSELL. Analyses of mustard, VII, 106
- PREYER. Occurrence of hæmoglobin, VIII, 506
- PREYER, A. Fermentation of cacao beans, VI, 686
- PRICE. Sausage, estimation of starch in, VIII, 374  
separation of coal-tar colours used in, VIII, 383
- PRIEST. See *Moor*.
- PRINGSHEIM. Estimation of sulphur in proteins, VIII, 80  
and GIBSON. Estimation of sulphur in proteins, VIII, 80
- PRIOR. Detection of sulphuring in hops, VII, 182  
Fermenting power of yeast, I, 222
- PROCHAZHA and ENDEMANN. Analysis of chick, IV, 161  
and HERMAN, H. N. Estimation of  $\beta$ -naphthol in the presence of large quantities of  $\alpha$ -naphthol, III, 256
- PROCTER. Berberine, solubility of, VI, 553  
Gelatin, water absorption of, VIII, 611  
Hide powder, standardising of, V, 79  
Leather, analysis of, V, 105  
Linseed oil, refraction constants of, IX, 192  
Marine animal oils, insoluble bromide value for, II, 29  
Phloroglucinol-tannins, detection of, V, 12  
Quercitannic acid, action of, on blood-albumin, V, 25
- Saccharin, estimation of, III, 435
- Tannin assay, V, 61, 68  
Eitner-Philip sulphide test for, IX, 404  
estimation of, VI, 615  
extracts, determination of colour in, V, 96
- and BENNETT. Insoluble brominated esters from whale and sperm oils, II, 240  
Insoluble bromides from linseed oil, II, 337  
Tannins, estimation of, V, 90
- HIRST. Oxidation method of tannin assay, V, 65
- HOLMES. Oxidation of oils by blowing, II, 365  
Refractive index of linseed oil, II, 338
- SEYMOUR-JONES. Estimation of free acid in tan-liquors, V, 98
- PROELSS. Salts of alkaloids, VI, 185
- PROLLUIS. Estimation of morphine in opium, VI, 419  
total alkaloids in cinchona bark, VI, 489
- PROLLUIS, F. Isinglass and fish-gelatin, VIII, 619
- PRZIBRAM. Paramyosinogen and myosinogen, VIII, 279
- PUBLOW. See *Van Slyke*.
- PUCKNER. Areca alkaloids, IX, 481  
Hydrastine, gravimetric estimation of, VI, 570  
Morphine-narcotine meconate, assay of, IX, 504
- PUCKNER, W. A. Effect of heat on caffeine, VI, 582
- PULFRICH. Refractometer, I, 22, 23

- PURDIE, T.** Preparation of active lactic acids, VII, 449  
**PURSEL.** See *Webster*.  
**PYMAN.**  $\beta$ -Iminazolyethylamine, synthesis of, VII, 350  
*Iso-pilocarpine*, constitution of, VII, 53  
*Pilosine*, IX, 537  
 See *Carr, Ewins, Jowett*.  
 and **REYNOLDS.** *Meteloidine*, VI, 301

## Q

- QUAJAT, E.** Ash of dry tobacco, VI, 243  
**QUANTIN, H.** Preparation of methylamine, VI, 13  
**QUAYLE.** See *Mabery*.  
**QUINCKE.** Estimation of potassium ferricyanide, VII, 529

## R

- VAN RAALTE.** Estimation of benzoic acid, IX, 284  
 of salicylic acid, IX, 303  
**RABAUT.** See *Aloy*.  
**RABE.** *Cinchona* alkaloids, constitution of, IX, 515  
*Hydrocinchonine*, rotation of, VI, 542  
 and **McMILLAN.** Preparation of *gnoscopine*, VI, 397  
**RABENAU.** Solubility of *guaiacum* in ether, IV, 65  
**RACE.** Beer, determination of the original gravity of, I, 156  
 estimation of the mineral constituents of, I, 160  
 See *Ross*.  
**DE RACZKOWSKI.** See *Bordas*.  
**RADCLIFFE.** Constants for *carnaúba* wax, II, 271  
**RADEMACHER, A.** Assay of commercial xylene, III, 220  
**RADENHAUSEN.** See *Danilewski*.  
**RADULESCU.** Morphine, colour test for, IX, 497  
**RAIKOW, P. N.** Benzoic acid, detection of chlorinated compounds in, III, 407  
*Halphen's* colour test for cottonseed oil, II, 135  
*Rose* oil, IV, 386, 387  
 congealing point of, IV, 385  
 and **SCHTARBONOW.** Detection of adulterants in antipyrine, VI, 44  
**RAIZISS and DUBIN.** Estimation of benzoic acid, IX, 283  
**RAKUSIN.** Rotation of castor oil, II, 160, 172  
**RAKUSIN, A.** Optical activity of kerosene, III, 135  
**RAKUSIN, M.** Flash point of linseed oil, II, 331  
**RAMBOE.** Bleaching of wax, II, 244  
**RAMMSTEDT.** See *Matthes*.  
**RAMSAY, CHICK and COLLINGRIDGE.** Action of chromic acid on gutta, IV, 158  
**RANE.** See *Bierry*.  
**RANSOM.** See *Dunstan*.  
**RANWEZ and CAMPIN.** *Ipecacuanhas*, classification of, VII, 43  
 spurious, VII, 49  
**RAPER.** Preparation of protein digestion products, VIII, 470  
**RAPP.** Yeast, coagulating enzyme, in, I, 212  
*zymase* in, I, 214  
 See *Buchner*.  
**RAQUET.** See *Caron*.  
**RASCH.** Analyses used in tartar works, I, 548  
 Fermentation test for lees, I, 551  
**RASCHIG.** Preparation of hydrazine sulphate, VI, 24  
**RASCHIG, F.** *m-Cresol*, estimation of, in cresol mixtures, IX, 273  
 separation of, from *o-* and *p-cresols*, III, 313  
**RASPE.** See *Bedford*.  
**RATH.** See *Mai*.  
**RATNER.** See *Olsen*.  
**RAU, H. M.** Estimation of indigotin, v, 402  
**VON RAUMER.** Detection of rancidity in meat fat, VIII, 318  
 Iodine value of lard and its fatty acids, II, 392  
**RAVENEL, HASTINGS and HAMMER.** Effect of low temperatures on milk, VIII, 144  
**RAVENNA.** See *Ciamician*.  
**RAWLE.** Calorimeter, III, 51  
**RAWSON.** Indigo, brown substances in, v, 389  
 estimation of, IX, 428  
 yellow, v, 389  
*Indigotin*, estimation, v, 394, 395, 396, 401  
*Indirubin*, extraction of, v, 397  
*Magenta*, detection of, in orchil and cudbear, v, 428  
*Naphthol* yellow, estimation of, v, 480  
*S*, assay of, v, 128  
 Wool-fat, estimation of unsaponifiable matter in, II, 500  
 See *Knecht*.  
**READ, E. A.** Tea, detection of colour in, IX, 454, 529  
 See *Dunstan*.  
**REBIÈRE.** Analysis of metallic benzoates, III, 412  
 Composition of mercuric benzoate, III, 415  
**REBS, H.** Identification of acaroid resins, IV, 17  
**REDMAN.** See *Rhodes*.  
**WEITH and BROCK.** Estimation of phenols in essential oils, IX, 327  
*Phenol*, bromination of, IX, 271  
**REDWOOD.** Classification of the more volatile portions of American petroleum, III, 111  
 See *Archbutt, Deering, Graham*.  
**REDWOOD, B.** Caucasian petroleum, distillation of, III, 45  
 Oils, effect of temperature on the viscosity of, III, 148  
*Ozokerite*, products of distillation of, III, 56  
*Paraffin* scale, machine for testing, III, 194  
 Petroleum and air, proportion of, required to produce dangerous explosions, III, 120  
*Rape* oil, specific gravity of, II, 127  
 Russian and American kerosenes, fractional distillation of, III, 129  
**REDWOOD, ROBERT.** Apparatus for colour test for kerosene, III, 131  
**REED.** Estimation of benzoic acid in catsup, III, 414  
**REES.** Characterisation of *saccharomycetes*, I, 210

- REEVE, CHARLES S. and LEWIS, RICHARD H.  
Tars, dimethyl sulphate test applied to,  
IX, 278
- REFORMATZKY. Isolation of linoleic acid from  
linseed oil, II, 351
- REGNAULD, J. Presence of carbon oxychloride  
in commercial chloroform, I, 276
- REGNAULT. Assay of petroleum by distillation,  
III, 50
- REHFUSS. See *Bergeim*.
- REHNSTROM, A. W. Substitute for coffee, VI, 664
- REICHARD. Berberine hydrochloride, tests for,  
VI, 559  
Cinchonine, reaction of, with Fröhde's re-  
agent, VI, 201  
Digitonin, reactions of, IX, 546  
Hydrastinine, IX, 524  
Morphine, test for, VI, 381, 382  
Narceine, narcotine and papaverine, colour  
tests for, VI, 370  
Opium, assay of, VI, 428  
Pilocarpine and concentrated sulphuric  
acid, reaction of, VI, 199  
Salicylic acid, test for, IX, 299  
Santonin, reactions of, VII, 154  
Sparteine, colour tests for, VI, 235  
Thebaine, colour tests of, VI, 406  
Triacetyl aconitine, VI, 262  
Yeast, nitrogenous constituents of, I, 208
- REICHARDT. Pseudo-morphine as a transforma-  
tion product of morphine in the body,  
VI, 405, 437
- REICHARDT, C. Tests for cocaine, VI, 325
- REICHEL and SPIRO. Compounds which retard  
rennet coagulation, VIII, 130
- REICHELMAN and LEUSCHER. Detection of  
colouring matters in foods, V, 651
- REICHERT. Determination of the Reichert  
value for fats, II, 22  
Hæmoglobin, preparation of, VIII, 508
- REICHL. Detection of glycerol, II, 454  
and BREINL. Distinction between dextrin and  
arabin and bassorin, I, 439
- REID. Linoleum, II, 362  
Linseed oil, change in composition of, in  
linoleum manufacture, II, 346  
drying of, II, 344  
Saccharin, estimation of, III, 434
- REID, W. Molecular weight of oxyhæmoglobin,  
VIII, 507
- REIJST. See *Wijsman*.
- REIMER. See *Tiemann*.  
and WILL. Presence of di-erucin in rape oil, II,  
123
- REINBOLD. See *Häfner*.
- REINGRUBER. See *Emmert*.
- REINITZA. Phytosterol from roots of carrots, II,  
485
- REINITZER. Composition of Siam benzoin, III,  
449  
Gum benzoin, IX, 294
- REINKE and RODEWALD. Phytosterol from  
*æthaliu septicum*, II, 485
- REISCHAUER. See *Hersfeld*.
- REISSIGER. See *Lippert*.
- REIZ. Ripeness for cheese, VIII, 249
- REMSSEN. See *Fahlberg*.  
and BURTON. Saccharin, estimation of, III, 434  
reactions of, III, 430
- REMY. Bouillon cubes, IX, 617  
Estimation of benzoic acid, IX, 283  
of resins in hops, VII, 176
- REMYS, C. Effect of alcohol on the specific  
gravity of chloroform, I, 280
- RENARD. Arachidic and lignoceric acids, solu-  
bility of, IX, 126  
Arachis oil, detection and estimation of, II, 93  
percentage of arachidic acid isolated from,  
II, 96
- RENARD, A. Composition of rosin oil, IV, 39  
spirit, IV, 37
- RENDLE, T. See *A. R. Ling*.
- RENNIE, E. H. Dinitroquinine, VI, 509
- RENTSCHLER, M. J. Effect of hydrogen peroxide  
on milk, VIII, 690
- REPITON. Mineral acids in vinegar, IX, 94
- REUTER. Chloral-antipyrine, VI, 46  
*p*-phenetidin, detection of, in phenacetin, VI,  
100
- REUTER, L. Distinction between naphthalene  
and naphthols, III, 254
- REUTTER. See *Tschirck*.
- REVERDIN and FULDA. Naphthalene and its  
sulphonic acids, III, 244, 252  
and DE LA HARPE. Estimation of methylamine,  
VI, 92
- REVIS, C. Benzoic acid, detection of, IX, 280  
Butter, difference figure for, IX, 625  
See *E. R. Bolton, Burnett*.  
and BOLTON, E. R. Butter fat, II, 279; IX, 152  
constants for, II, 290  
Ghee, IX, 175  
Milk products, VIII, 179; IX, 597  
Margarine, IX, 166
- BURNETT. Estimation of starch in cocoa, IX,  
73
- PAYNE. Milk, condensed, estimation of  
sugars in, IX, 597  
Salicylic acid, estimation of, in butter, II,  
313  
in cream, III, 485; VIII, 195  
in milk, III, 485
- REYCHER.  $\beta$ -Derivatives of camphor, IV, 202
- REYCHLER. Camphene dibromide, IV, 183
- REYNOLDS. See *Carr, Pyman*.
- RHEINBERGER. See *Heiduschka*.
- RHODES and REDMAN. Phenol, bromination of,  
IX, 271
- RIBAN. Action of ferric chloride on dipentene  
dihydrochloride, IV, 174  
Specific gravity of *l*-pinene, IV, 179  
See *J. H. Long*.
- RICE, C. Antiseptic principle in wood-tar, III,  
346
- RICEVUTO. Precipitation of gelatin by tannin,  
VIII, 590
- RICHARD, P. Behaviour of wool with coal-tar  
colours, VIII, 687
- RICHARDS and GIES. Elastin, VIII, 91  
PALMER. Estimation of tannin, V, 89

- RICHARDSON.** Glycerol, boiling point of, II, 447  
vapour tensions of, IX, 211  
Holde's method for the estimation of the amount of hard paraffin scale in oils, III, 82  
Meat, canning of, VIII, 330  
Mineral oils, determination of sulphur in, IX, 247  
Nitrogen, estimation of, in the cold water extract of meat, VIII, 300  
Saltpetre, use of, in the curing of meat, VIII, 363  
Silk, estimation of, VIII, 649, 650  
mulberry, analysis of, VIII, 633  
and **AYKROYD.** Estimation of sulphur compounds in soap-lye glycerine, II, 469  
**JAFFE.** Estimation of glycerol, II, 460, 466  
Suitability of olive oil for oiling wood, II, 111  
**SHERUBEL.** Beef, extraction of, with water and solutions of salts, VIII, 303  
Meat, ammoniacal nitrogen in, VIII, 315  
chilled, VIII, 349  
cold water extract of, VIII, 299  
frozen, deterioration of, VIII, 312  
**WALLACE.** Sulphur in Texas petroleum, III, 40  
**RICHARDSON, C.** Asphalts, absence of oxygen in, III, 90, 91  
analysis of, III, 63, 69, 73, 75  
bromine absorption of, III, 92  
fluxes, III, 95  
hydrocarbons in, III, 93  
pavement, modern, III, 67  
Asphaltic materials, determination of the melting and softening points for, III, 32  
Bituminous road materials, tests for, III, 101  
Non-bituminous matter, absorption of, by clay, III, 84  
Trinidad asphalt, composition of, III, 61  
**RICHARDSON, P. W.** Formula of silk fibroin, VIII, 636  
and **GREGORY, J. C.** Estimation of tartaric acid in cream of tartar, IX, 103  
**WALTON, W.** Analysis of camphorated oil, IV, 201  
**RICHARDSON, W. D.** Meat and meat products, VIII, 261  
**RICHARDSON, W. R.** Tartrazin, v, 133  
**RICHE and BARDY.** Detection of ethyl alcohol in wood naphtha, I, 103  
Estimation of methyl alcohol in the presence of ethyl alcohol, I, 98  
**HALPHEN.** Test for distinguishing between the products of Russian and American petroleum, III, 136  
**RICHMOND.** Casein, estimation of, IX, 596  
Cream, aldehyde figure for, IX, 599  
composition of, VIII, 182  
Manila copal, IX, 310  
Milk, analysis of, VIII, 142, 159, 163, 182  
composition of separator slime from, VIII, 183  
detection of the addition of water to, VIII, 165  
**RICHMOND.** Milk, dried, analysis of, VIII, 239, 240  
estimation of fat in, VIII, 149, 152  
proteins in, by the aldehyde number, VIII, 154  
homogenised, analysis of, VIII, 221  
skim, composition of, VIII, 182  
Zeiss butyro-refractometer, II, 282  
See *Hehner, Vieth.*  
and **BOSELEY.** Separation of proteins in milk, VIII, 156  
**HARRISON.** Estimation of boric acid in butter, II, 312  
**MILLER.** Butter, estimation of boric acid in, II, 312  
Cream, estimation of boron compounds in, VIII, 194  
Milk, estimation of borates in, VIII, 174  
of proteins in, VIII, 154  
**RICHMOND, H. D.** Estimation of lactose in milk optically, I, 369  
Rate of distillation of acetic acid homologues, I, 519  
**RICHMOND, S. O.** Constants for colophony, IV, 26  
**RICHTER.** Berberine, estimation of, IX, 521  
Cinchona alkaloids, titration of, IX, 514  
See *Bohrisch.*  
**RIDEAL and STEWART.** Gelatin, action of chlorine on, VIII, 591  
bacterial decomposition of, VIII, 598  
Meat-extract, assay of, by bromine precipitation, VIII, 421  
Proteins, precipitation of, VIII, 397  
**RIDENOUR.** Analyses of cacao beans, VI, 687  
Analysis of cocoa nibs, VI, 689  
**RIEHELMANN.** See *Forster.*  
**RIEGL.** See *Weller.*  
**RIEGER, J. B.** See *W. Salant.*  
**RIEGLER.** Estimation of phenol, III, 303  
Reactions of saccharin, III, 431  
**RIEGLER, E.** Estimation of uric acid, VII, 372  
**RIELÄNDER.** Ergot, formation of cadaverine in, VII, 348  
of putrescine in, VII, 347  
**VAN RIJN, J. J. L.** Carpaine, VII, 1  
 **Rimini.** Estimation of hydrazine, VI, 26  
Simon's test for phenylhydrazine, VI, 34  
 **RIMMINGTON.** Microscopical examination of pepper, VII, 67  
 **RIMMINGTON, F. M.** Removal of the colouring matter from coffee, VI, 673  
 **RIMPEL.** See *Harries.*  
 **RINTOUL.** See *Nathan.*  
 **RIPPER.** Estimation of acetaldehyde, VII, 439  
of aldehydes, I, 256; III, 419  
of ketones, III, 419  
 **RIPPETON.** Test for asafetida, IX, 318  
 **RIPPETON, J.** Alkaloids in belladonna leaves, VI, 313  
 **RISSE.** See *Semmler.*  
 **RITTER.** Esters of phytosterol with the higher fatty acids, II, 489  
Isolation of cholesterols II, 489



- RITTHAUSEN. Estimation of the total proteins in milk, VIII, 153  
Phytosterol from wheat gluten, II, 485
- RITSERT, E. Test for the purity of commercial acetanilide, VI, 84
- RIVA-ROCCI, S. Estimation of albumose and peptone, VIII, 396
- RIXON. See *Nierenstein*.
- ROAF. Molecular weight of proteins, VIII, 77  
Use of Barfoed's reagent to show the hydrolysis of lactose and maltose by enzymes, I, 333  
See *Moore*.
- ROBBINS. Alkaloid from green hellebore, VII, 81
- ROBERTS. Determination of the diastatic power of enzymes, VIII, 4  
See *Barcroft*.
- ROBERTS, CHAS. C. Distinction between crude and distilled glycerin, II, 476
- ROBERTS, WM. (SIR). Quadri-urates, VII, 373
- ROBERTSON. Casein, compounds of, with calcium and sodium, VIII, 124  
determination of the refractive index of, VIII, 136  
solubility of, in salts, VIII, 124  
Nitration of cellulose, III, 560  
Sulphuric esters in gun cotton, III, 569  
Will test for explosives, III, 615  
See *A. W. Blyth, Pennington*.  
and *HOFFMANN*. Examination of written characters for the detection of forgeries and alterations, V, 677
- NAPPER. Estimation of nitrogen peroxide produced by the decomposition of nitro-explosives I, 39
- SMART. Abel test for explosives, III, 595
- ROBERTSON, J. W. See *G. A. Burrell*.
- ROBERTSON, W. Higher fatty acids, II, 370
- ROBIN. Casein, precipitation of, from milk, III, 478
- ROBIN, L. Benzoic acid, detection of, III, 410; IX, 282  
Coconut oil, detection of, in butter, lard and cacao butter, II, 180, 284
- ROBIN, M. Test for morphine, VI, 381
- ROBINSON. See *Perkin*.  
and *GOODWIN*. Quinoline bases, VI, 155
- ROBINSON, H. H. Gum of *Cochlospermum gossypium*, I, 445  
Gums, I, 440
- ROCH. Detection of albumin, III, 504
- ROCHLEDER. Acid from rhubarb, V, 230  
Fat of coffee, VI, 647
- ROCQUES. Estimation of acetaldehyde, I, 266  
of glycerol in wines, I, 167
- RODANO, G. A. See *G. Armani*.
- RODELLA. Microscopical examination of cheese, VIII, 259
- RODER, TH. Estimation of the alkaloid in fluid-extract of coca, VI, 344
- RODEWALD. See *Reinke*.
- RODINOFF. Test for dionine, VI, 390
- ROEDER. Gravimetric estimation of hydrastine, VI, 570
- RÖMER. See *Schunck*.
- ROESER. Estimation of mustard oil, VII, 109
- ROESLER and GLASMANN. Estimation of benzidine and toluidine, VI, 109
- ROEWER. Preparation of dinitromonochlorhydrin, III, 575
- ROGERS. Ipecacuanha alkaloids, IX, 542  
Preparation of sodium cyanide, VII, 472
- ROGERSON, H. See *F. B. Power*.
- ROGIER and FIORE. Quinine glycerophosphate, IX, 518
- ROGOZINSKI. Protein digestion products, VIII, 470
- ROHDLICH. See *Matthes*.
- ROHMANN and SPITZER. Indophenol test for oxydases, VIII, 13
- ROJAHN. See *von Soden*.
- ROLLETT. Composition of linolenic acid, IX, 185  
Preparation of oxyhæmoglobin, VIII, 507
- ROMANIS, R. Ash of Indian and Burmese tobacco, VI, 243
- V. ROMBURGH and DE HAAS, T. Gutta-percha, IV, 158  
and *LOHMANN*. Composition of the ash from tea, VI, 606
- ROMIJN. Iodometric method for the estimation of formaldehyde, I, 261
- ROMIJN, G. Defection of gelatin in formogelatin, VIII, 601
- RONA and MICHAELIS. Isoelectric points and relative acidity constants of proteins, VIII, 89  
See *Michaelis*.
- RONNET. Detection of caramel in vinegar, IX, 96
- ROOS. See *Hinsberg*.
- ROOS, VAN HAMEL. Re-roasting of coffee-berries, VI, 670  
Tin in canned foods, VIII, 338
- ROOS, L. Estimation of tannins, V, 93
- ROQUES. See *Léger*.
- RORIVE. See *Tollens*.
- ROSENBACH, O. Detection of indirubin in urine, VII, 256
- ROSENBERG. Hydrastine, VI, 564  
See *Semmler*.
- ROSENBLOOM. Acetone, detection of, IX, 577  
Bile, analyses of, IX, 579  
Morphine, toxicology of, IX, 508  
See also *Kahn*.
- ROSENBURG. See *Herzog*.
- ROSENDAHL. Alkaloids from *aconitum septentrionale*, VI, 277
- ROSENGREN. Rancidity of butter, IX, 165
- ROSENHEIM. Putrid placenta, *p*-hydroxyphenylethylamine in, VII, 346  
isoamylamine in, VII, 345  
and *KAJURA*. Absence of prolamin in rice, VIII, 107
- SCHIDROWITZ. Optical activity of gallic and gallotannic acids, III, 531; V, 19  
Solubility of gallic acid, III, 527
- ROSENMUND. Synthesis of hordenine, VII, 36  
of *p*-hydroxyphenylethylamine, VII, 347
- ROSENSTEIN. See *Lewin*.
- ROSENSTIEHL. Distinctions between *o*-, *m*- and *p*-toluidine, VI, 65  
Formation of lactic acid in wine, VII, 430



ROSENTHALER. Adulteration of Peruvian balsam, III, 458  
 Estimation of hydrocyanic acid in essential oils, IX, 326  
 and GÖRNER. Berberine, reaction of, IX, 521  
 ROSER. Constitution of cotarnine, VI, 358  
 of narceine, VI, 360  
 ROSS and RACE. Almond and apricot-kernel oils, IX, 129  
 ROSSEL. Aloin test for blood, VIII, 524  
 ROSSITER. See *Armstrong*.  
 ROSSMANN. See *Schönfeld*.  
 ROST, FRANZ and HEISE. Spectrum of hæmoglobin, VIII, 514  
 ROTA, A. G. Analysis of dyestuffs, v, 464  
 Detection of colouring matters from meat products, VIII, 383  
 Separation of mixed dyestuffs, v, 475  
 ROTH. See *Kreis, Paal*.  
 ROTHERA. Modification of Legal's sodium nitroprusside test for acetone, VII, 402  
 Piturine, IX, 482  
 ROTHMUND. Solubility of triethylamine in water, VI, 20  
 ROUSSIN, Z. Separation of gum arabic and dextrin, I, 442  
 ROWE. See *Gill, Hargreaves*.  
 ROZSENYI. Estimation of cereal substitutes in coffee, IX, 531  
 RUBINSKY. Bacteriology of koumiss, VIII, 226  
 RUBNER, M. Meat extracts, VIII, 396  
 RUDLING, A. Constants for resins, IV, II, 14  
 Venice turpentine, IV, 77, 78  
 RUDOFF. See *O. Fischer*.  
 RUDORFF. Influence of water on the melting point of glacial acetic acid, I, 493  
 RÜBSAMEN. Isolation of morphine from animal matter, VI, 438  
 RÜDEL. Berbamine, composition of, VI, 56  
 Berberine, VI, 551, 552  
 Oxyacanthine, VI, 561  
 RÜDORFF. Determination of the strength of glacial acetic acid by its solidifying point, II, 62  
 RÜHELE. Detection of saponins in beverages, VII, 129  
 RÜMLER. Betasterol from beet root, II, 487  
 RUGGERI. See *Tortelli*.  
 RUHEMANN. Colour test for proteins, VIII, 41  
 RUHSAM, R. Dégras, iodine value for, II, 505  
 examination of, II, 509, 510  
 RUNG. See *Bins*.  
 RUNG, C. See *W. Grotrian*.  
 RUNNE. Use of phenolphthalein as an indicator in the estimation of alkaloids, VI, 181  
 RUPE. Citronellal, IX, 341, 344  
 RUPP. Belladonna and its preparations, assay of, VI, 316  
 Berberine, estimation of, IX, 527  
 Hydrastine, estimation of, VI, 570; IX, 524  
 Hydrazine, estimation of, VI, 26  
 and SCHIEDT. Estimation of thiocyanates, VII, 555  
 RUPP, E. Estimation of mercury in mercuric salicylate, III, 489

RUSSELL. See *Coombs*.  
 and HODGSON. Analyses of vinegar, IX, 92  
 RUSSIG, F. and FORTMANN, G. *m*-Cresol, estimation of, in cresol mixtures, IX, 274  
 RUSTERHOLZ and MILLIKIN. Examination of dyed fibres, v, 486  
 RUTTEN. Estimation of naphthalene in coal gas, IX, 266  
 RUTTEN, J. See *W. P. Jorissen*.  
 VAN RYN. See *Grutterink*.  
 RYNISKA, A. Detection of picric acid, III, 585

## S

SAAL. See *Tschirch*.  
 SAARE. Culture yeast, I, 215  
 SABATIER and SENDERENS. Origin of bitumens, III, 37  
 SABIN. Linseed oil, drying of, IX, 199  
 oxidation of, II, 346  
 SABRAZÈS and GUÉRIVE. Toxic action of hordenine, VII, 37  
 SACHS. Cacao butter, substitutes for, II, 179; VI, 720  
 Coconut stearine, constants for, II, 190  
 Palm-nut stearine, II, 196  
 SACHSSE. Estimation of dextrose by an alkaline solution of potassium mercuric iodide, I, 337  
 and KORMANN. Estimation of amino-compounds in plant-products, VII, 238  
 SACHSSE, R. Estimation of asparagine in plant-products, VII, 237  
 SACK and TOLLIUS. Alstol and lupeol, II, 488  
 SACKUR. See *Laqueur*.  
 SADIKOFF. Collagen, VIII, 91  
 Gelatin, VIII, 91  
 SADTLER. Aniline and its allies, VI, 51; IX, 472  
 Anthracene and its associates, III, 261  
 Arachis oil, properties of, II, 91, 92  
 Asphalt, estimation of water in, III, 74  
 fractional separation of the constituents of, III, 87  
 Bitumens, III, 37; IX, 240  
 Camphor, crude, examination of, IV, 197  
 Cinnamic aldehyde, estimation of, III, 442  
 Kerosene emulsions, analysis of, III, 141  
 Lemon oil, estimation of aldehydes in, IV, 275  
 estimation of citral in, IV, 353  
 Lubricating oil, mineral, estimation of fatty oils in, III, 169  
 Petroleum, crude, extraction of solid paraffin from, III, 51  
 distillation of, III, 107  
 Phenols, III, 287; IX, 270  
 Pitch, coal-tar and water-gas, differences between, III, 33  
 Rock-asphalt, composition of, III, 61  
 SADTLER, S. P. Bitumens, oxygen in, IX, 250  
 Cocaine, VI, 321, 494  
 Creosote for preserving timber, specifications for, III, 367  
 and S. S. Liebermann-Storch test, application to butter and butter substitutes, II, 316  
 SAGE. Newfoundland codliver oil, II, 214

- SAGE, E. Analyses of tea, VI, 602
- SAGEMAN, P. J. See *J. J. Fox*.
- SALAMON and SEABER. Glyceryl acetate in essential oils, IX, 333
- SALANT, W. and RIEGER, J. B. Toxicity of caffeine, IX, 528
- SALKOWSKI. Dextrose, detection of, in urine, I, 398  
 Hæmatoporphyrin, occurrence of, in urine, VIII, 555  
 Inositol, detection of, IX, 609  
 Meat extracts, IX, 615  
 Phytosterol from adulterated codliver oil, II, 485  
 Protein digests, examination of, VIII, 484  
 Uric acid, estimation of, VII, 368  
 Yeast, cell wall of, I, 206  
   cellulose, I, 209  
   gum, IX, 16  
 See *Niebel*.
- SALKOWSKI, E. Albumose in hen's egg albumin, VIII, 433  
 Purine bases, estimation of, VII, 325
- SALM. Phenolphthalein, dissociation constant of, V, 264
- SALMON and AMOS. Value of seeds in some varieties of hops, VII, 190
- SALMONOWITZ. Myoctonine, VI, 276
- SALOMON. Specific gravity of corresponding solutions of cane sugar and anhydrous dextrose, I, 294  
 maltose, I, 295
- SALOMON, P. Specific gravity of sugar solutions, I, 289
- SALOMON, G. Crystalline silver compounds with guanine, carnine, adenine and episcarine, VII, 323
- SALOMONE. Action of fuming nitric acid on abrastol, III, 401
- SALWAY. Cotarnine, synthesis of, VI, 358, 397  
 Escramine, VII, 30  
 Eserine, VII, 24  
   blue, VII, 25  
 Eseroline, rubreserine and eserine blue, VII, 26  
 Physostigma seeds, assay of, VII, 28  
 Physovenine, VII, 30  
 Sitosterol-*d*-glucoside, IX, 545  
 See *Power*.
- SALZBERGER. Protoveratrine, VII, 87
- SALZBERGER, G. Alkaloids from the Hellebores, VII, 79
- SALZER. Detection of aniline in antifebrin, VI, 85
- SAMUELY. See *Abderhalden*.
- DE SANCTIS, G. Composition of wool-fat, II, 496
- SANDERS. See *Norris*.
- SANDERS, J. McC. Petroleums, heavy, specific gravity of, IX, 247
- SANDMANN. Impurities in india rubber, IV, 107
- SANFELICI. Ripening of cheese, VIII, 257
- SANGER. See *Graham-Smith*.
- SANGLÉ-FERRIÈRE. Detection of abrastol, III, 402
- SANI, G. Phytosterol from olive oil, II, 486
- SANSONI. Effect of the administration of phenyl urethane, VI, 88
- SAPOJNIKOW. Classification of nitrocellulose, III, 562
- SATIE. See *Jeancaud*.
- SAUL, J. E. Detection of dextrose in commercial tannin, V, 21  
 Test for eserine, VII, 26
- SAUNDERS, E. C. Preparation of pure oleic acid, II, 402
- SAVORY. See *Hopkins*.
- SAWAMURA. Tea, IX, 528
- SAWITSCH. Rennet-enzyme, VIII, 126, 129
- SAWJALOW. Plasteins, VIII, 495  
 Rennet-enzyme, VIII, 126, 129
- SAWYER. Removal of excess of lead from sugar solutions clarified with lead acetate, I, 311  
 See *Davis*.
- SCARLATA. See *Mancuso-Lima*.
- SCHAAL. Composition of Japan wax, II, 192
- SCHACHT. See *Grün*.
- SCHAEGLER. Arachis oil, solidifying point of, II, 91  
 Cameline oil, II, 132  
 Candle nut oil, use of, II, 148  
 Creso seed oil, II, 139  
 Linseed oil, composition of, II, 329  
 Maize oil, solidifying point of, II, 140  
 Oils, fats and waxes, yields of, II, 4  
 Rape oil, solidifying point of, II, 123  
 Tea-seed oil, II, 119
- SCHAEFER. Ethyl-morphine, IX, 500  
 Test for the purity of cocaine, VI, 334
- SCHAEFER, G. L. Anhydrous quinine, IX, 516
- SCHÄFER. Estimation of aloin in aloes, VII, 147
- SCHÄFER, L. Test for commercial quinine sulphate, VI, 526
- SCHAEFFER. Cheese, estimation of iron in, VIII, 258  
 fat content of, VIII, 254
- SCHÄFFER. Presence of casein in milk in combination with tri-calcium phosphate, VIII, 119  
 See *Folin*.
- SCHAEER. Aloin test for blood, VIII, 524  
 Berberine, test for, VI, 555  
 Chloral hydrate as a solvent for blood stains, VIII, 570
- SCHÄRGES. See *Lerch*.
- SCHAMMEL, L. R. Preparation of cineol, IV, 285
- SCHARDINGER, F. Production of *l*-lactic acid, VII, 449
- SCHARLING. Constitution of arctic sperm oil, II, 241
- SCHAUWECKER. See *Harries*.
- SCHIEBLER. Average composition of the ash from beet sugar, I, 349  
 Estimation of ash from cane sugar, I, 345  
 See *Mategczek*.
- SCHIEJ. Glycerol, boiling point of, II, 447  
 Palmitin, II, 397  
 Stearin, II, 401
- SCHELL. Detection of mangrove in quebracho extract, IX, 398

- SCHELLENS.** See *Fischer*.
- SCHENCK.** Water content of sausage, IX, 619  
and **BURMEISTER.** Detection of cinnamic acid, IX, 292
- SCHERER.** Inositol, detection of, IX, 608  
Keratoids, VIII, 673  
Leucine, reaction of, VII, 230  
Mucin, analysis of, VIII, 628
- SCHERING.** Manufacture of piperazine, VII, 198  
Production of vanillin from eugenol, III, 515
- SCHERNING.** Estimation of nitrogen in protein digests by the use of tin salts, VIII, 485
- SCHERTEL.** Preparation of potassium platino-cyanide, VII, 534
- SCHERUBEL.** See *Richardson*.
- SCHESTAKOFF.** Bone fat, II, 205  
Free acid in tallow, II, 210  
See *Shukoff*.
- SCHEURER-KESTNER.** Estimation of the sulphonated and non-sulphonated acids in turkey-red oil, II, 170
- SCHIDROWITZ.** Caramel, Amthor's test for, V, 656  
detection of, in wines, I, 179  
India-rubber latex, analysis of, IX, 320  
physical tests for, IV, 113  
tensile properties of, IV, 118  
Opium, assay of, VI, 426, 428  
Potable spirits, estimation of furfural in, I, 197  
higher alcohols in, I, 188, 192  
Whiskies, analysis of, I, 199  
See *Rosenheim*.
- and **GOLDSBROUGH.** Viscosity of india rubber, IV, 109
- KAYE.** Acetone extraction of rubber, IV, 123  
Potable spirits, estimation of higher alcohols in, I, 189, 190, 192  
Whiskey, distillation of, I, 202
- SCHIEDT.** See *Rupp*.
- SCHIFF.** Amines, estimation of, VI, 9  
Specific gravity of solutions of potassium ferricyanide, VII, 525  
ferrocyanides, VII, 505  
Urea, test for, VII, 293
- SCHIFF, H.** Aspartic acid, preparation of, from asparagine, VII, 240  
Gallotannic acid, synthesis of, V, 16  
Tannins of galls, V, 4  
Turpentine oil, commercial, IV, 403
- SCHILBACH.** See *Schmidt*.
- SCHILLING.** See *Marcusson*.
- SCHIMIDZER.** Extraction of fat in animal tissues, IX, 223
- SCHIMMEL.** Buchu oil, IX, 353  
Separation of geraniol and citronellol, IV, 265  
Test for mustard oil for pharmaceutical purposes, VII, 110
- SCHIMMEL AND CO.** Acaroid resins, constants for, IV, 17  
Almonds, oil of bitter, III, 421  
Amber, oil of, IV, 21  
Angelica oil, IX, 350  
Aniseed oil, terpenes in, IX, 351, 352  
Borneol, IX, 342  
Cadinene, IX, 315
- SCHIMMEL AND CO.** Camphor oil, IV, 321, 323  
Cassia oil, adulteration of, III, 445  
Cedar-leaf oil, IV, 327  
Cedar-wood oil, IV, 326  
Celery oil, IV, 327  
Chamomile oil, German, IV, 329  
Chenopodium oil, IV, 427  
Cineol, estimation of, IV, 286, 341  
Cinnamic aldehyde, estimation of, III, 441  
Cinnamon oil, sesquiterpene from, IX, 357  
Citronella oil, estimation of geraniol and citronellal in, IV, 267  
Clove oil, IV, 330, 331  
Coriander oil, IV, 332  
Dextrophellandrene in angelica oil, IV, 310  
Dill oil, IV, 335  
Essential oils, methoxyl numbers of, IV, 242  
Eugenol, estimation of, IV, 297  
Glyceryl acetate, detection of, in essential oils, IX, 332  
Hyssop oil, IV, 345  
Juniper oil, IV, 345, 346  
Lavender oils, IV, 348, 349; IX, 363, 364  
Lemon oil, IV, 354  
Lemon-grass oil, estimation of aldehydes in, IV, 234  
Linalol oil, detection of camphor in, IX, 367  
Linalol, IX, 341  
Linalyl acetate in bergamot oil, IV, 317  
Menthol, IV, 283  
Methyl anthranilate in neroli oil, IV, 367  
Mustard oil, estimation of allyl-thiocarbimide in, IV, 301  
Nutmeg oil, IV, 358  
Odoriferous substances, solubility table of the, IV, 460  
Orange oils, IV, 359, 360, 361  
Pennyroyal oil, IV, 377  
Peppermint oils, distillation of, IV, 374  
Japanese, IX, 370  
Pimento oil, IV, 378  
Rose oil, IV, 383, 384, 386, 387, 389  
Rosemary oil, IV, 390  
Sandalwood oil, IV, 393  
Spear-mint oil, IV, 376  
Spike-lavender oil, IV, 351  
Terpinyl acetate, detection of, IX, 331  
Wormwood oils, IV, 428
- SCHINDELMEISER.** Alkaloids, solubility of, in carbon tetrachloride, IX, 496  
Test for nicotine, VI, 239  
See *Kondakow*.
- SCHINDLER and WASCHATA.** Percentage of linseed oil from various linseeds, II, 324
- SCHIRNER.** Estimation of potassium iodide, IX, 612
- SCHITTENHELM.** See *Abderhalden*.
- SCHJERNING.** Nitrogen, estimation of, in meat bases, VIII, 301  
Proteins, estimation of, VIII, 53  
precipitants of, VIII, 397
- SCHLAGDENHAUFFEN.** See *Heckel*.
- SCHLICHT.** Estimation of mustard oil, VII, 108
- SCHLICHTING and WINTHER.** Yeast, IX, 15
- SCHLICHTING, EMIL.** Yeast I, 205

- SCHLICKUM, O. Application of De Vrij's chromate test to quinine sulphate, VI, 526
- SCHLOESING. Tobacco alkaloid, IX, 478
- SCHLOSSBERGER. Chemical composition of yeast, I, 208
- SCHLOSSMANN. Precipitation of casein with alum, VIII, 133
- SCHLOTTERBECK. Berberine, VI, 552
- SCHLUMBERGER. Estimation of naphthalene in coal gas, IX, 267, 268
- SCHMATOLLA. Test for benzoic acid, IX, 282
- SCHMATOLLA, O. Separation of camphor from alcohol, IV, 200
- SCHMIDT. Alkaloids, function of, in plants, IX, 478
- Apomorphine hydrochloride, VI, 388
- test for, VI, 388
- Canadine, preparation of, from hydrastine, VI, 574
- Codeine hydrochloride, VI, 391
- Datura metel, alkaloids in, VI, 320
- Horse flesh, testing for, VIII, 273
- Hydrastine, VI, 564
- Meat, identification of species of, VIII, 276
- See *Abderhalden, Majeri, Tiemann*.
- and BARTH. Melting point of protocathechuic acid, III, 512
- DAVIS. Inactive lupanine, VI, 228
- KERSTEIN. Hydrastine hydrochloride, VI, 571
- Hyoscine in Datura, VI, 299
- LÖWENHARDT. Picrotoxin, VII, 160
- SCHILBACH. Oxidation of berberine, VI, 554
- SCHMIDT, E. Atropine sulphate, VI, 296
- Berberine, purification of, VI, 553
- tendency of, to combine with neutral solvents, VI, 554
- Caffeine, action of hydrochloric acid on, VI, 584
- Gelsemic acid, VII, 34
- Glue, detection of, IX, 605
- Stramonium seeds, alkaloids in, VI, 319
- SCHMIDT, R. E. Colouring matter in lac-dye, V, 425
- VON SCHMIDT and ERBAN. Colophony, constants for, IV, 26
- Copals, constants for, IV, 55
- Mastic, IV, 49, 50
- Resins, constants for, IV, 10, 12, 13
- Sandarac, IV, 58
- Shellac, solubility of, IV, 68
- Venice turpentine, constants for, IV, 77
- SCHMIDT-NIELSEN. Rennet-enzyme, VIII, 126, 129, 130
- SCHMIEDEBERG. Chondroitin-sulphuric acid, IX, 575
- Onuphin, VIII, 92
- Potatoes, poisoning by, VII, 93
- Salicylic aldehyde test for oxydases, VIII, 14
- See *Bunge*.
- SCHMITT. Reichert value for fats and oils, II, 23
- and HIEPE. Differentiation of malic, tartaric and succinic acids in wines, I, 187
- NASSE. Formation of *p*-hydroxyphenyl-methylamine from tyrosine, VII, 347
- SCHMITZ. Estimation of nitrogen in rubber, IX, 322
- See *Emden*.
- SCHMITZ-DUMONT, W. Substitute for hide powder, V, 86
- VON SCHMOELLING. Cedar nut oil, II, 150
- SCHNECHENBURGER. See *Windaus*.
- SCHNEEGANS and GEROCK. Detection of free salicylic acid in oil of wintergreen, III, 496
- SCHNEIDER. Cyanates, detection of, in commercial cyanide, VII, 539
- India-rubber, test for the quality of, IV, 114
- Indigo, extraction of, IX, 429
- Indigotin, estimation of, V, 393
- Lactic acid, separation of, from other organic acids, VII, 436
- and BLUMENFELD. Porpoise oil, II, 231
- Vikare seal oil, II, 227
- SCHNELL. Iodine values for arachis oil, II, 92
- See *Lintner*.
- SCHOEN, G. A. Estimation of *p*-toluidine in admixture with *o*-toluidine, VI, 69
- SCHÖNBEIN. Guaiacum test for blood, VIII, 522
- SCHÖNDORFF and WACHHOLDER. Glycogen in fish, IX, 622
- SCHÖNE and TOLLENS. Presence of lactic acid in molasses, VII, 429
- SCHÖNFELD, HINRICHS and ROSSMANN. Top fermenting yeast, IX, 15
- and HIRT. Yeast, IX, 15
- SCHOEPP, R. J. L. Effect of maltol on the ferric chloride test for salicylic acid, III, 478
- SCHOLL. See *Greifenhagen*.
- SCHOLTEN, C. Test for ferric acid, VII, 416
- SCHOLZE. See *Wolf*.
- SCHOOP. Methylaniline in dimethylaniline, VI, 95
- See *Loebisch*.
- SCHOOP, P. Aniline and *p*-toluidine, specific gravity of, VI, 78
- Colouring matters, determination of, by their absorption spectra, V, 438
- o*- and *p*-Toluidine, separation of, VI, 69
- SCHOORL. Separation of various organic acids VII, 436
- SCHORAS. Precipitation of Prussian blue by sunlight, VII, 507
- SCHORM. Effect of light on pure coniine, VI, 213
- SCHORM, J. Extraction of coniine from hemlock VI, 221
- SCHRADER. See *Curtius*.
- SCHREFELD. Use of normal lead acetate in clarifying sugar solutions, I, 311
- SCHREIBER. Estimation of sulphur in meat, VIII, 298
- and TABER. Estimation of tin in canned foods, VIII, 344, 346
- ZETESCHE. Examination of turpentine oil, IV, 422
- SCHREINER. Benzidine test for oxydases, VIII, 14
- Spermine, composition of, VII, 203
- phosphate, preparation of, from human semen, VII, 202
- See *Kremers*.

- VON SCHRENK. Suitable composition of creosote oil for preserving timber, III, 369
- SCHRODT. Use of hydrogen peroxide and borax as a preservative, VIII, 691
- VON SCHRÖDER. Formogelatin, preparation of, VIII, 601  
Gelatin, precipitation of, by tannin, VIII, 590  
Narceine, VI, 399  
Tannin assay, oxidation method of, v, 63  
See *Counciler, Grillo*.  
and BARTEL. Extraction of tannins, v, 2
- SCHRÖDER, M. J. Detection of acetanilide in phenacetin, VI, 102
- SCHROETER. See *Nietzki*.
- SCHRÖTER. See *Trimble*.
- SCHRÖTTER. Melting point of mastic, IV, 59  
and BRISSON. Specific gravity of mastic, IV, 59
- SCHRUMPF. Pepsin, VIII, 491
- SCHRYVER. Chlorophyll, v, 638  
Cholalic, choleic and deoxycholeic acids, separation of, VII, 418  
Globulins and albumins, difference between, VIII, 33  
plant, extraction of, VIII, 61  
Ox bile, acid from, IX, 579  
Phenols, estimation of, III, 302; IV, 226  
Phenyl ethers of camphoric acid, IV, 205  
Proteins, IX, 592  
and albuminoid substances, VIII, 17  
digestion products of the, VIII, 467  
estimation of, by coagulation by alcohol, VIII, 56  
identification of, by their solubilities, VIII, 77  
precipitation of, by salts, VIII, 37  
Tin, estimation of, in canned meat, VIII, 343
- SCHTARBONOW. See *Raikow*.
- SCHUCH. Zeisel and Fanto's method for the estimation of glycerol, II, 463
- SCHÜLER. Isolation of linoleic acid from linseed oil, II, 350
- SCHÜTTE. Alkaloids in belladonna, VI, 312
- SCHÜTZENBERGER. Decomposition of wool with baryta, VIII, 685  
and BOURGEOIS. Composition of chondrin, VIII, 625  
IONINE. Russian petroleum, III, 42
- SCHULTZ. Purity of beet sugar, I, 352
- SCHULTZE. Phosphoantimonic acid as a reagent for alkaloids, VI, 188  
See *Wagner*.  
and MAXWELL. Galactan mannan and pentosans in coffee, VI, 645
- SCHULZ. Globin, VIII, 91  
Hæmatoporphyrin, occurrence of, in urine, VIII, 554  
Oxyhæmoglobin, hydrolysis of, VIII, 544  
Saponin glucosides of sarsaparilla, VII, 128  
See *Curtins, Zsigmondy*.
- SCHULZE. Aconine, oxidation product of, VI, 265  
Aconitine, composition of, VI, 259  
Ammonium thiocyanate, preparation of, VII, 544  
Asparagine, estimation of, VII, 237
- SCHULZE. Ether residue, separation of the constituents of, II, 494  
Ethyl-benzaconine, VI, 265  
Glycerol, estimation of, II, 463  
 $\alpha$ - and  $\beta$ -naphthols, occurrence of, in the green oils from coal-tar, III, 252  
See *MÄRCKER*.  
and BARBIERI. Caulosterol, II, 487  
from lupins, II, 488  
Phytosterol, from triticum vulgare, folium perenin, II, 485
- BIERLING. Alkaloids of aconitum vulpafia, IX, 488
- BOSSHARD. Isolation of glutamine, VII, 242  
Leucine, VII, 230
- FRANKFURT. Isolation of betaine and choline in malt-culms and wheat-germs, VII, 279
- LIEBNER. Alkaloid obtained from aconitine, IX, 487
- LIXIERNIK. Extraction of lecithin from plants, VII, 283  
Varieties of leucine, VII, 230
- TRIER. Yeast nucleic acid, VIII, 73
- WINTERSTEIN. Effect of exposure to air on the melting point of phytosterol, II, 489
- SCHULZE, E. Isolation of asparagine and glutamine from vegetable juices, VII, 239  
Reaction of guanidine salts with Nessler's reagent, VII, 305
- SCHULZE, F. Estimation of glycerol, comparison of methods, II, 465
- SCHULZE, K. E. Estimation of pyridine, VI, 138
- SCHUMACHER-KOPP, E. Analyses of Maggi's meat preparations, VIII, 396
- SCHUMANN. See *Ware*.
- SCHUMM. Spectrum of hæmoglobin, VIII, 515
- SCHUMM, O. Guaiacum test for blood, VIII, 523, 524  
and WESTPHAL, C. Benzidine test for blood, VIII, 524
- SCHUNCK. Indiretin and indihumin, v, 389  
Melting point of alizarin, v, 207  
and MARCHLEWSKI. Chlorophyll, v, 638  
Phylloporphyrin, VIII, 556  
RÖMER. Analysis of alizarin paste, v, 217
- SCHUPPLI. See *Baragiola*.
- SCHUTT, F. T. Cocoa husks, VI, 696
- SCHUTTE, O. Estimation of fatty acids in soap, IX, 206
- SCHUTZENBERG. Formation of copper and iron carbonyl-ferricyanides in the destructive distillation of coal, VII, 532
- SCHWABE. Use of antipyrine, VI, 42
- SCHWALB. Separation of paraffin hydrocarbons from beeswax, II, 243
- SCHWALBE. Estimation of the cupric reducing power of cellulose, I, 432, 433  
Tests for artificial silk, VIII, 665
- SCHWARZ. Reaction for orcinol, v, 427
- SCHWARTZ, H. Detection of acetanilide in phenacetin, VI, 101
- SCHWARZ. Elastin, analysis of, VIII, 631  
Asphalt, estimation of, IX, 246  
See *Pinner*.

- SCHWARZE and VON HUBER. Mineral oils, estimation of paraffin in, IX, 257
- SCHWARZ, F. Coal-tar distillates, detection of natural asphaltum and petroleum pitch in, IX, 277
- Separation of asphaltic compounds from hydrocarbon oils, IX, 231
- SCHWEDES, L. See *C. Mannich*.
- SCHWEINITZ and EMERY. Heat of combustion of fats and oils and their adulterants, II, 45
- SCHWEISSINGER. Gerrard's test for atropine, VI, 306
- Phytosterol from rape oil, II, 486
- SCHWEITZER. Copaivic acid, IV, 5
- Sugar in cacao beans, VI, 703
- and LUNGWITZ. Hübl process for the estimation of the iodine value of fats and oils, II, 31
- Lard oil, relation between the iodine value and congealing point for, II, 199
- specific gravity of, II, 198
- Lubricating oils, detection of mineral matters in, III, 163
- Whale oil, II, 229
- SCHWEITZER, C. Cocoa red, VI, 699
- SCOCCHIANTI. See *Moriari*.
- SCOTT. See *Spence, Aders Plimmer*.
- SCOTT, G. E. See *A. H. Allen*.
- SCOTT-SMITH. See *Allen*.
- SCOTT-SMITH, G. E. Extraction of caffeine from tea, VI, 610
- SCOTTISH MINERAL OIL ASSOCIATION. Assay of paraffin scale, III, 192
- Examination of heavy mineral oils, III, 172
- SCRIBANI, F. D. Adulteration of lemon juice with nitric acid, I, 564
- SCUDDER. Detection of methyl alcohol, I, 90
- See *Mulliken*.
- and BIGGS. Test for methyl alcohol, I, 89
- SEABER. See *Salamon*.
- SEAR, F. Separation of palmitic and oleic acids, II, 405
- SEARL. Detection of yeast-extract, VIII, 417
- SEARLE. See *Allen*.
- SEARLE, A. B. Action of bromine on gelatin, VIII, 592
- SEBELIEN. Milk-albumin, VIII, 131
- Globulins, VIII, 91
- Milk-globulin, VIII, 131
- SÉC and BOCKFONTAINE. Toxic action of cinchonamine sulphate, VI, 547
- SECHLER and BECKER. Detection of ammoniacum and galbanum in asafoetida, IX, 316
- SEE, G. Action of sparteine sulphate, VI, 233
- SEEKER, ALBERT F. Colouring matters in foods, V, 623
- SEIDEL. See *Blumenfeld*.
- SEIDEL, F. See *E. Müller*.
- SEIDELL. Estimation of salicylates, IX, 304
- salicylic acid, III, 482
- See *Ulzer*.
- SEIDELL, A. Estimation of thymol in essential oils, IX, 327
- Solubility of caffeine, VI, 583
- salol in various solvents III, 294
- SEIDENBERG, A. Gelatin, detection of, IX, 600
- SEIDL. Detection of inositol, IX, 609
- SEIFERT. Formation of lactic acid in wine, VII, 430
- Pure yeast culture in wine, I, 218
- SEIGER, M. Assay of cresol soap, IX, 208
- SEIGFELD. Action of formalin on milk, VIII, 125
- SEITZ. See *Bullnheimer*.
- SELF. Test for salicylic acid, IX, 299
- See *Harrison*.
- SELMI. Arsenical ptomaine, VII, 355
- SEMBRITZKY. Formation of a skin on milk, VIII, 125
- SEMMLER. Diosphenol, IV, 299
- d*-Linalol in coriander oil, IV, 332
- Mace oil, composition of, IV, 359
- Phellandrene, isomerides of, IV, 177
- Vetivenol, IX, 347
- and RISSE. Sesquiterpene from cinnamon oil, IX, 357
- ROSENBERG. Constituents of camphor oil, IX, 354
- THOMS, H. Myristicin in mace oil, IV, 359
- SPORNITZ. Calamenenol, IX, 353
- Sesquiterpene from citronella oil, IX, 346
- SEMMLER, F. W. Allyl sulphide, IV, 300
- Formation of *iso*-dihydro-camphene from *iso*-borneol, IV, 279
- and MAYER, E. W. Sesquiterpene from clove oil, IX, 358
- SENDERENS. See *Sabatier*.
- SENFT. Berberine and hydrastine, detection of, IX, 521
- SENGER, O. Absinthiin, VII, 157
- SENIER and LOWE. Borax test for glycerol, II, 454
- SENER. Haemase, VIII, 15
- SERENA. Colour reactions of opium alkaloids, VI, 366
- SERGER. Creatinine in bouillon cubes, IX, 617
- Estimation of salicylic acid, IX, 303
- SERRE. Commercial aloin, VII, 142
- SESTINI, F. and L. Fermentation of uric acid, VII, 364
- SETTERBERG. Determination of the strength of glue, VIII, 613
- SEYDA, A. Test for tannins, V, 9
- SEYEWETZ. See *La mière*.
- SEYFFERT.  $\gamma$ -Resin from hops, VII, 167
- SEYMOUR-JONES. See *Procter*.
- SHAFFER. Preparation of lactic acid from sugar, VII, 430
- SHAFFER. Estimation of  $\beta$ -hydroxybutyric acid in urine, VII, 403
- and MARRIOTT.  $\beta$ -Hydroxybutyric acid, IX, 578
- SHARWOOD. Alkali zinc cyanide, VII, 476
- SHAW. Estimation of fat and salt in butter, IX, 158
- and ECKLES. Formulæ for the analysis of milk, VIII, 164
- Lactometer, VIII, 145
- SHEDDEN. Berberine phosphate, VI, 561
- SHELBOURNE. See *Coste*.
- SHENK. See *Dunlap*.
- SHENSTONE.  $\alpha$ - and  $\beta$ -Barbaloin, VII, 139



- SHENSTONE, W. A.** Apparatus for distillation, I, 18
- SHEPHEARD.** See *Dunstan*.
- SHEPPARD.** Linseed oil, IX, 181
- SHERBATSHEV, D.** Detection of cocaine and its substitutes, IX, 495
- SHERMAN.** Presence of maltol in baked cereal products and roasted coffee, III, 478  
See *Hinkel*.  
and **FALK.** Blown oils, IX, 201  
Linseed oil, influence of atmospheric oxidation on the constants for, II, 336  
oxidation of, II, 346
- GRAY and HAMMERSCHLAG.** Comparison of the calculated and determined viscosity numbers and flashing and burning points in oil mixtures, III, 147
- and **GROSS.** Test for salicylic acid, IX, 300
- KENDALL and CLARK.** Determination of diastatic power, VIII, 3, 5
- and **SNELL.** Acidity of lard oil, II, 198  
Heat of combustion of linseed oil, II, 339  
of oils and fats and their adulterants, II, 45
- SHERMAN, H. C.** Assay of acetate of lime, I, 508
- SHERUBEL.** See *Richardson*.
- SHIMOYAMA.** Atisine, VI, 278
- SHIMOYAMA, B.** Solubility of quinine herepathite, VI, 513
- SHINOSAKI.** Peppermint oils, IX, 370
- SHORT.** See *Dunstan*.
- SHORT, F. W.** Optical rotation of copaiba oil, IV, 87
- VON SHRENK, HERMAN.** Specifications for creosote, III, 368
- SHREVE.** Opium, estimation of morphine in, IX, 504
- SHREWSBURY, H. S. and KNAPP, A. W.** Formaldehyde, estimation of, in milk, VIII, 172  
test for, in milk, I, 259
- SHUKOFF.** Bone fat, II, 205  
Determination of the solidification points of fats and oils, II, 57  
Soja-bean oil, II, 146  
and **SCHESTAKOFF.** Estimation of glycerol, II, 463
- SIAU, R. L. and PAVY, F. W.** Detection of acetone in urine, I, 106
- SIDERSKI.** Vacuum drying oven, I, 69
- SIEBER.** See *Nencki*.
- SIEBERT.** Hyoscyamine in *Anisodus luridus*, VI, 289
- SIEBOLD, L.** Determination of specific gravity by means of hydrometers, I, 7  
Relative solvent action of solutions of lithium sodium and potassium carbonates on uric acid, VII, 378
- SIEBURG.** Strophanthic acid, IX, 547
- SIEGFELD.** Analyses of sterilised milk, VIII, 222  
Mean molecular weights of soluble and insoluble fatty acids from butter, II, 287  
and **KEISTEN.** Buttermilk, VIII, 196
- SIEGFELD.** Acids in butter fat, IX, 152
- SIEGFRIED.** Acetyl-lactic acid, production of, from flesh, VII, 452  
Gelatone, analysis of, VIII, 595  
Protein digestion products, preparation of, VIII, 470  
Reticulin, VIII, 92
- SIEMSEN, H.** Cocaine, detection of, VI, 323, 326
- SIEVERS, A. F.** Strychnos alkaloids, IX, 510
- SIGMUND.** Compounds which retard rennet coagulation, VIII, 130
- SILBER.** See *Ciamician*.
- SILBERMANN.** Silk, artificial, test for, VIII, 669  
constitution of, VIII, 637  
mulberry, analyses of, VIII, 633  
Silk-weighting, VIII, 654, 655, 656  
See *Vignon*.
- SILBERRAD, ABLETT and MERRYMAN.** Estimation of nitroglycerin, III, 572
- SILBERSTEIN.** See *Bardach*.
- SILLER, R.** Hops, estimation of resins in, IX, 554
- DA SILVA, F.** Cocaine, application of Vitali's test for atropine to, VI, 325  
Eserine, test for, VII, 26  
Furfuraldehyde test for Douro olive oil, II, 145  
Lafon's reagent, colour reactions of, with opium bases, VI, 369  
Salicylic acid in wines, detection and extraction of, III, 477, 478
- SILVERMANN.** See *Winton*.
- SIMAND.** Dégras, examination of, II, 506, 507, 508, 509  
Dégras, former, II, 505  
See *Kohnstein*.
- SIMAND, P.** Tannin assay, oxidation method of, V, 61  
extracts, analysis of, V, 32
- SIMMER.** Salts of alkaloids, VI, 185
- SIMMONDS.** Detection and estimation of methyl alcohol in the presence of ethyl alcohol, IX, 1  
Separation of strychnine and quinine, IX, 518
- SIMMONS.** See *Hudson-Cox*.
- SIMMONS, W. H.** Refractive index of eugenol, IV, 330
- SIMON.** Detection of phenylhydrazine, VI, 33
- SIMONS.** See *Crampton*.
- SINABALDI.** Detection of abrastol, III, 403
- SINDALL and BACON.** Manufacture of wood-pulp, IX, 81  
See *Kraemer*.
- SINDALL, R. W.** Paper and paper-making materials, I, 465
- SINGH, PURAN.** Vetivert oil, IX, 348
- SISLEY.** See *Vignon*.
- SISLEY, P.** Tannins, action of various reagents on, V, 15  
estimation of, V, 66
- SjöQUIST.** Measurement of the changes of electrical conductivity of acidic and basic solutions of proteins, VIII, 88
- SJOLLEMA.** Linseed oil, refractive index of, II, 338  
solidification of, II, 331



- SKALWEIT. Specific gravity of butter and its adulterants at various temperatures, II, 285
- SKALWEIT, J. Specific gravity of coffee extracts, VI, 661
- SKELTON. See *Plimmer*.
- SKETCHLEY, N. P. See *O. Hehner*.
- SKITA. See *E. Fischer*.
- SLATOR. Formation of lactic acid in wine, VII, 430
- VAN SLYKE. Amino-acids, estimation of, in urine, VII, 408
- Amino-groups, determination of, IX, 560, 561
- Amino-nitrogen, estimation of, in protein digestion products, VIII, 486
- Casein, preparation of, VIII, 117
- Cheese, American cheddar, analysis of, VIII, 250
- examination of the nitrogenous compounds in, VIII, 256
- Monamino-acids, estimation of, VII, 263
- Nitrogen, arginine, histidine and lysine, estimation of, VIII, 32
- estimation of, in the hydrolysis products of proteins, VIII, 82
- Proteins, modified, and amino-derivatives, estimation of, VIII, 157
- See *Bosworth, Levens*.
- and BOSWORTH. Casein, IX, 595, 596
- estimation of, volumetrically, VIII, 133
- HARDING and HART. Action of rennet-enzyme in cheese, VIII, 128
- HART. Calcium-casein, VIII, 123
- Composition of the curd of sour milk, VIII, 122
- Formation of *p*-hydroxyphenylethylamine in cheddar cheese, VII, 346
- PUBLOW. Cheese, ripening of, VIII, 244
- VAN SLYKE, L. L. Proteins of milk, VIII, 113, 114, 115; IX, 595
- VAN SLYKE, L. L. and D. D. Casein, acetic acid as a precipitant for, VIII, 131
- action of acids on, VIII, 122
- SMALL. Determination of the acidity of hide powder, V, 81
- Formaldehyde test for tannins, IX, 402
- SMALL, F. H. Analysis of spent bark, IX, 394
- SMART. See *Robertson*.
- SMEDLEY. Acids in butter fat, IX, 152
- SMETHAM. Analyses of feeding stuffs, VIII, 93; IX, 594
- Tallow, iodine value of, II, 211
- and DODD. Constants for colophony, IV, 26
- SMETHAM, A. Cocoa husks, VI, 696
- SMITA. See *Paschkis*.
- SMITH. Benzaldehyde, estimation of, IX, 286
- Keratin, solubility of, VIII, 675, 676
- Lard, analysis of, II, 95
- Maize oil, solidifying point of, II, 140
- Opium, assay of, VI, 424
- Wool-grease, distilled, II, 502
- See *Baker, Chapman, Chittenden, Colman, Leonard, Mabery, Teschemacher*.
- and FREY. Estimation of phenol-*p*-sulphonic acid, IX, 279
- SMITH and TUTTLE. Iodine value for linseed oil, IX, 188
- WADE. Constants for myrtle wax, II, 195
- SMITH, ALBERT. Detection of chicory in coffee, VI, 672
- SMITH, A. W. Cider-vinegar, I, 497
- SMITH, B. H. See *J. K. Haywood*.
- SMITH, E. S. Measurement of jelly strength of glue, VIII, 607
- SMITH, H. G. Aromadendral, IV, 336
- Eucalyptus oils, IV, 245, 338, 339, 342
- SMITH, H. L. Estimation of tannin in tea, IX, 529
- SMITH, H. M. See *N. Leonard*.
- SMITH, T. and H. Meconoisin, VI, 411
- Xanthaline, VI, 406
- SMITH, WATSON. Anthracene, estimation of, in coal-tar, III, 286
- Blast-furnace tar, composition of the distillate from, III, 18
- Creosote oil, III, 362, 363
- Diglyceryl triphthalate, preparation of, III, 544
- Hydrocarbons, solid, detection of, by their reactions with antimonous and bismuthous chloride, III, 277
- $\beta$ -Naphthaquinone, reactions of, with resorcinol, naphthols and phenol, III, 338
- Prussian blue, solubility of, in hydrochloric acid and alcohol, VII, 507
- Soap, estimation of water in, II, 424
- Wool, microscopical characters of, VIII, 681
- SMITH, W. H. See *J. B. Tuttle*.
- SMOOT. Chestnut-oak bark, IX, 396; 400
- SMORODINZEW. Meat extracts, IX, 615
- SNELL. See *Sherman*.
- SNODGRASS. See *Mills*.
- SNOW. Iodine value of essential oils, IV, 239, 240
- SNOW, H. W. Salts of caffeine, VI, 589
- SNYDER. Composition of the ash of wheat flour, I, 456
- Gliadin ratio in flour, I, 455
- SOBEL. Acetone, estimation of, IX, 577
- VON SODEN. Amyrol in sandalwood oil, IV, 396
- and ROJAHN. Sandalwood oils, IV, 396
- VON SODEN, H. African copaiba oil, IX, 315
- SOEHNE. See *Boehringer*.
- SÖLDNER. Calcium casein, VIII, 119, 123
- SÖRENSEN. Peptin digestion products, examination of, VIII, 478
- Protein digests, preparation of, VIII, 480
- hydrolysis, measurement of, VIII, 10
- Meat, decomposition of, IX, 612
- Monamino-acids, estimation of, VII, 262
- Urine, estimation of amino-acids in, VII, 408
- HENRIQUES and GJALDBAEK. Measurement of protein hydrolysis, VIII, 10
- and JESSEN-HANSEN. Hydrolysis of protein digestion products, VIII, 489
- SOLDAINI. Lupanine, VI, 228
- SOLLEY. See *Chittenden*.
- SOLOMINA. White fulminate of mercury, III, 588
- SOLOWJEW. See *London*.
- SOLTSEIN. Arachis oil, presence of sesame oil in, II, 101
- Atropine, poisoning by, VI, 310

- SOLTSEIN.** Butter, rancidity of, II, 313  
 Lard, Halphen's test for cottonseed oil applied to, II, 321  
 Sesame oil, test for, II, 145
- SOMMARUGA.** Socotrine aloes, VII, 139
- SOMMER.** Hydrazine, estimation of, IX, 470  
 Production of vanillin from eugenol, III, 515
- SOMMER, F.** Action of formaldehyde on paraffins, IX, 238
- SONCINI.** See *Molman*.
- SONNENSCHN.** Formula for gelsemine, VII, 32  
 Reagent for alkaloids, VI, 187
- SORBY.** See *Hodgkinson*.
- SORBY, H. C.** Absorption-spectra of colouring materials, V, 437
- SORET, J. L.** Spectrum of hæmoglobin, VIII, 514
- SORNET.** See *Dalépine*.
- SOSTEGNI and CARPENTIERI.** Detection of coal-tar colours in food, V, 642; VIII, 382
- SOUBEIRAN and DELONDRE.** Composition of maté, VI, 642
- SOURDEVAL.** See *Marguerite*.
- SOXHLET.** Dextrose and levulose, action of, on Pehling's solution, I, 374  
 estimation of, with Sachse's mercuric solution, I, 338  
 Lactose, action of, of mercurial reagents, I, 366  
 Maltose, reducing power of, I, 362  
 Sugar solutions, influence of special conditions on the reducing power of, I, 336
- SPÄTH.** Detection of facing materials in coffee berries, VI, 652
- SPÄTH.** Black pepper, VII, 59  
 Ergot in flour, VII, 24
- SPÄTH, E.** Yolk of egg, VIII, 435
- SPALLINO.** Estimation of nicotine, IX, 486
- SPALTEHOLZ, W.** Estimation of phenols in soap, III, 323, 334
- SPENCE and GALLETTY.** Estimation of india-rubber, IX, 321  
 and **SCOTT.** Estimation of india-rubber, IX, 321  
**YOUNG.** Estimation of sulphur in rubber, IX, 323
- SPENCE, D.** India-rubber, analysis of, IV, 112, 113  
 composition of, IV, 108  
 globules, size of, IV, 105  
 latex, analysis of, IV, 106
- SPENCER.** Estimation of caffeine by Gomberg's process, VI, 612
- SPERLING.** Nitroantipyrine, VI, 42
- SPICA.** Citric acid, analysis of, IX, 112  
 Saccharin, detection of, III, 433  
 Salicylic acid, detection of, III, 477, 479  
 Sumac, adulteration of, V, 103
- SPIEGEL.** Alkaloids of Yohimboa bark, VII, 93  
 Formation of glycuronic acid from purrée, VII, 396
- SPIEGEL, L.** Gelseminine, VII, 33
- SPIERS, C. W.** Precipitation of tannin, IX, 393
- SPILKER.** See *Kraemer*.
- SPILLER.** See *Hopkins*.
- SPILLER, J.** Action of concentrated sulphuric acid on azo-dyes, V, 204  
 Examination of coal-tar dyes, V, 471
- VON SPINDLER, O.** Analysis of lime and lemon juices, IX, 110
- SPIRO.** See *Reichel*.  
 and **FULD.** Globulins, VIII, 91
- SPIRO, K.** Detection of hippuric acid, VII, 393
- SPITZER.** See *Hunsiker, Rohmann*.
- SPIVAK.** Analysis of kephyr, VIII, 231
- SPOHN.** See *Dragendorff*.
- SPORNITZ.** See *Semmler*.
- SPRENGEL.** Determination of specific gravity of liquids, I, 6
- SPRINGER.** Salts of alkaloids, VI, 185
- SPRINKMEYER.** Baudouin's test for sesame oil in the presence of rancid cottonseed oil, II, 301  
 Furfuraldehyde test in the presence of rancid oils, II, 144  
 and **DIEDRICH.** Kapok oil, IX, 136  
 Lard, detection of beef or mutton fat in, IX, 179  
 Linseed oil, hexabromide test for, IX, 191
- FÜRSTENBERG.** Refractive index of the fatty acids from butter, II, 283
- WAGNER.** Comparison of varieties of sesame oil, II, 143
- SPURGE, E. C.** Estimation of eugenol, IV, 297, 331
- SQUIBB.** Ether, detection of alcohol and water in, I, 230  
 Specific gravity of ethyl alcohol, I, 110  
 of mixtures of ethyl ether and alcohol, I, 228
- SQUIRE, E. R.** Aconite preparations, physiological assay of, VI, 282  
 Aconitine, commercial, VI, 287  
 Caffeine in guarana, VI, 683  
 Cinchona bark, red, assay of, VI, 486  
 Cocaine, crude, analysis of, VI, 328  
 Mydriasis by atropine, VI, 304  
 Opium, assay of, VI, 419
- SQUIRE.** Ammoniacum, IX, 315  
 Guaiacum, IX, 311  
 Hemlock, assay of coniine in, VI, 223  
 and **CAINES.** Estimation of salol, III, 497  
 Solubility of turpentine oil in acetic acid, IV, 409
- STABLER.** Spigeline, VI, 235
- STÄDELER.** Action of sulphuric acid on spongin, VIII, 672
- STADLINGER.** See *Lehman*.
- STAHLSCHMIDT.** Estimation of caffeine in tea, VI, 606
- STANDFORD, H. R.** Specifications for creosote oil, III, 369
- STANEK.** Estimation of choline in molasses, VII, 277  
 Inversion of cane sugar, IX, 44  
 Refractometer values for sugar solutions, IX, 21  
 See *Milbauer*.
- STANFORD, E. C. C.** Algin, VIII, 622, 624
- STANGE.** See *Holde, Thiele*.

- STANHOUSE. Procter classification of tannins, v, 6
- STANSELL. See *Presse*.
- STANTON, R. B. Asphalt for reservoir lining in California, III, 69
- STAPP, O. Aconite alkaloids, VI, 255  
Aconitum, species of, VI, 253  
Pseudaconitine, VI, 270
- STARK. Test for the beating time of pulp, IX, 88  
See *Millard*.
- STARK, A. C. Application of Vitali's atropine test to cocaine, VI, 325  
Test for antipyrine with nitrous acid, VI, 40
- STARKENSTRIN. Estimation of glycogen, IX, 608  
Hydroxycaffeine, VI, 595
- STAVELEY, W. W. Detection of cresylic acid in phenol, III, 317
- STEELE. See *Masson*.
- STEENBUCH. Porpoise oils, II, 231
- STEENSMA. Detection of antipyrine, VI, 43, 49
- STEIN. Examination of dyed fibre, v, 486
- STEIN, W. Test for the fastness of dyes, v, 482
- STEINEGGER. Milk, action of formalin on, VIII, 125  
estimation of proteins in, VIII, 154
- STEINER, I. Action of maltose on Pavy's ammoniacal cupric solution, I, 363  
Analyses of commercial starch sugars, I, 380  
See *C. Von der Heide*.
- STEKL. See *Hannß*.
- STELLING, C. Estimation of the non-gelatinous substances in glue, VIII, 612
- STELZER. See *Moscheles*.
- STENGER. See *Lewin*.
- STENHOUSE. Berberine, VI, 551  
See *Graham*.
- STEPHAN. See *Tschirch*.
- STEPHAN, K. Acid in sweet-orange oil, IV, 359  
Action of acetic anhydride on geraniol, IV, 262
- STEPHENSON. See *Howard*.
- STEPHANSON. See *Howard*.
- STEPPUHN. See *Gottlieb*.
- STERN. See *Krapps*.
- STEUDEL. Nucleic acids, VIII, 72
- STEVENS. Assay of aconite alkaloids, VI, 280  
Physiological test for aconite, VI, 283  
See *Beadle*.
- STEVENS, A. B. Assay of opium, VI, 425, 426, 427
- STEVENSON. Analysis of pepper, VII, 63
- STEWART. See *Rideal*.
- STEWART, S. Detection of dammar resin, IX, 311
- STIASNY. Non-tans, value of, in tanning, v, 83  
Quebracho, analysis of, IX, 398  
Sulphite-cellulose and neradol D, distinction between, IX, 410  
Tannins, tests for, IX, 401, 402, 405  
See *Paniker*.
- STIEFEL. Estimation of glycerol, II, 466
- STIEHL, W. Condensation products of the aldehydes of essential oils with acetone, IV, 238
- STIEPEL. Insoluble bromide from linseed oil, IX, 120
- STILES and BATES. Bacteriological examination of eggs, VIII, 451
- STILES, G. W. Bacteriological examination of eggs, VIII, 450
- STILLWELL. Assay of acetate of lime, I, 508  
and GLADDING. Assay of acetate of lime, I, 508
- STILLWELL, C. M. Coefficient of expansion of olive oil, II, 50
- STINGL. See *Morawski*.
- STOCK. Crystallisation of lard, II, 321, 322  
See *Piloty*.
- STOCK, W. F. K. Analysis of pepper, VII, 65
- STOCKER. Test for balsam, IX, 296
- STOCKERT. See *Zeisel*.
- STOCKMAN. Cocaine hydrochloride, solubility of, in chloroform, VI, 327  
poisonous properties of, VI, 322
- STOCKMAN, R. Benzoyl-ecgonine, VI, 336  
Cocaine, amorphous, VI, 342  
Hygrine in coca leaves, VI, 343
- STOCKY, A. Isolation of vanillin from wine vinegar, III, 516
- STODDART. Estimation of tannins, v, 85
- STOEDELER. Detection of alcohol in chloroform, I, 279
- STOEDER. Pomegranate alkaloids, VI, 230
- STOEHR. Strychnine-disulphonic acid, VI, 443
- STOEPEL, P. Detection of adulterants in elemi, IV, 96
- STOHMANN, KLEBER, LANGBEIN and OFFENHAUER. Table of the heat of combustion of oils and fats, II, 45
- STOKES. Alizarin, detection of, by its absorption-spectrum, v, 213  
Gelatin, detection of, VIII, 166, 593  
and BODNER. Use of citric acid for the inversion of sugar in milk, I, 370
- STOKES, A. W. Detection of long pepper in true pepper, VII, 67
- STOKVIS. See *Jaarsveld*.
- STOLLE. Estimation of hydrazine, VI, 26  
Use of the Pulfrich refractometer in estimating sugars, I, 316
- STOLTZENBERG. Betaine hydrochloride, preparation of, from molasses residues, IX, 563
- STONE and WRIGHT. Estimation of starch, IX, 71
- STOOKEY. Preparation of protein digestion products, VIII, 470
- STOREK. See *Lauber*.
- STORER. See *Warren*.
- STORY-MASKELYNE. Carnaúba wax, II, 270
- STRACHE. See *Benedikt*.
- STRASSER. See *Donath*.
- STRAUCH. Composition and structure of silks, VIII, 642
- STRAUS. Physostigmine, IX, 536
- STRAUSS. See *Abderhalden*.
- STRECKER. Melting point of caffeine, VI, 581
- STREET. Bouillon cubes and soups, IX, 618  
Meat extracts, IX, 613
- STREET, JOHN PHILLIPS. Meat and meat products, IX, 607
- STRITAR and ZEIDLER. Estimation of methyl alcohol, I, 92

- STROHL.** Iodine absorption of cocoa butter, vi, 702
- STROHMER.** Specific gravity of aqueous solutions of glycerol, ii, 448
- STROPPIA.** See *Vitali*.
- STRUTHERS.** See *Marsh*.
- STUDER.** See *Tschirch*.
- STURCKE.** Composition of carnauba wax, ii, 270
- STUTZER.** Bovril, composition of, viii, 399  
Cocoa powders, analyses of, vi, 692  
Coffee berries, detection of sugar glazing on, vi, 652  
Meat-extracts, viii, 396, 397  
    estimation of gelatin in, viii, 415  
Peptones, viii, 396  
Proteins, estimation of, viii, 51  
Yeast. Nitrogenous constituents of, i, 208  
    See *Herfeldt*.  
and GAY. Lupine flakes, ix, 482  
    WINDISCH. Estimation of higher alcohols in potable spirits, i, 191
- SUDENDORF.** Refractive index of the fatty acids from butter, ii, 283  
    and LAHRMANN. Estimation of creatine and creatinine, ix, 610
- SÜVERN.** Reactions of nitrocellulose artificial silk, viii, 668
- SUIDA.** See *Liechti*.
- SUJIYAMA.** Camphor oil, iv, 322
- SULMAN, H. S.** Use of cyanogen bromide for renovating cyanide solutions, vii, 501
- SUNBERG.** Coconut oil in butter fat, ix, 153
- SUSS.** Occurrence of salicylic acid in strawberries, iii, 466
- SUTCLIFFE.** Hexabromide test for linseed oil, ix, 192  
    Insoluble bromide test for fats, ix, 118
- SUTERMEISTER, E.** Analysis of black liquors, ix, 83
- SUTO.** See *Kumagawa*.
- SUTTON.** Detection of colouring matters in canned vegetables, v, 651
- SUTTON, F.** Percentage of oil in mustard, vii, 113
- SUZUKE, HASTINGS and HART.** Cheddar cheese, viii, 242
- SVOBODA, H.** Detection of picric acid, v, 123
- SWAIN.** Kynurenic acid, ix, 569
- SWART.** See *de Bloeme*.
- SWAVING.** Reichert-Meissl values for Danish butter, ii, 284
- SWINTON.** See *Umney*.
- SWISS SOCIETY OF ANALYSTS.** Silver nitrate test for cottonseed oil, ii, 136
- SWOBODA.** Estimation of fatty acids by titration, ii, 376
- Sy.** Explosives, explosion test for, iii, 614  
    German 135° test for, iii, 613  
    Vieille test for, iii, 613  
    Maple products, tests for the adulteration of, i, 390  
    U. S. Army Ordnance 115° test for nitrocellulose powders, iii, 616
- SYKES, W. J. and MITCHELL, C. A.** Analyses of malt extract, i, 145
- SYMES, C.** Rotation of turpentine oil, iv, 406
- SZOMBATHY.** Apparatus for the estimation of oils and fats, ii, 4  
    Soxhlet's apparatus, i, 77
- SZTANKAY.** Composition of diuretin, iii, 491
- SZYMANSKI, F.** Peptone, viii, 396
- T**
- TABER.** See *Schreiber*.
- TAFFE.** Test for salicylic acid, iii, 476
- TAFTS.** See *Gill*.
- TAGGART.** See *Cross*.
- TAGLIAVINI.** Detection of saccharin in foods and beverages, iii, 433
- TAKAMINE.** Determination of the diastatic power of enzymes, viii, 5  
    See *Mills*.
- TAKAYAMA, J.** Japanese tea, preparation of, vi, 597  
    tobacco, analysis of, vi, 248  
    ash of, vi, 243  
    Tea, analyses of, vi, 600
- TAKEUCHI.** Estimation of urea by the use of urease, vii, 301
- TAMBA.** See *Hilger*.
- TAMBOR.** See *Kostanecki*.
- TAMMANN.**  $\alpha$ - and  $\beta$ -Methylnaphthalenes in paraffin, iii, 251
- TANGL.** Composition of casein, viii, 120
- TANKARD.** Estimation of sulphur in vulcanised rubber, iv, 141  
    Resins in Parà rubber, iv, 111  
    See *Allen*.
- TANKARD, A. R.** Meat, composition of, viii, 264  
    Nitric acid test for myrrh, iv, 99  
    Venice turpentine, constants for, iv, 78
- TANNER.** Saffron, v, 419
- TANRET.** Ergosterol, ii, 487, 488  
    Ergothioneine, vii, 20  
    Ergotinine, vii, 16  
    Pomegranate, alkaloids of, vii, 50  
    separation of, vi, 230
- TANRET, C.** Peptones, viii, 396
- TAPIS.** Use of iodesin in the estimation of alkaloids, vi, 183
- TAPIS, N. DE FUENTES.** See *G. Frerichs*.
- TAPPEINER and NEUNER.** Physiological action of harmaline, vii, 36
- TARBOWA and HARDY.** Phytosterol from roots of *echinophora spinosa*, ii, 486
- TARDY.** Terpeneol in anise oil, iv, 311  
    See *Bouchardat*.
- TARTAR, H. V. and BRADLEY, C. E.** Hops, estimation of resins in, ix, 555
- PILKINGTON, B.** Hops, antiseptic power of, ix, 553
- TARTARINOFF, P.** Gelatone, viii, 595
- TARUGI.** Preparation of potassium cyanate, vii, 537
- TARUGI, N.** Detection of cinchonine in quinine hydrochloride, ix, 517
- TASSILY.** Examination of Japan wax, ix, 118
- TATE, A. NORMAN.** Fatty acids, combining weights of, ii, 380  
    Palm oil, analysis of, ii, 185  
    Tallow, free acid in, ii, 210

- TATLOCK and THOMPSON.** Coffee, tannin in, VI, 645  
**and THOMSON.** Coffee, composition of, VI, 644  
 essence, analysis of, VI, 679  
 extracts, chicory in, IX, 532  
 fat values of, VI, 647  
 specific gravity of infusions of, VI, 661  
 Chicory, analysis of, VI, 672, 679  
 Hops, estimation of tannin in, V, 91  
 Lead, test for, in commercial tartaric acid, IX, 101  
 Tea, analyses of, VI, 600, 604  
 after infusion, VI, 625  
 estimation of caffeine in, VI, 609  
 of extract from, VI, 622  
 of tannin in, V, 91; VI, 619
- TÄUBER.** Driers, II, 360  
**and NORMAN.** Dyes from  $\beta$ -naphtholmonosulphonic acid, V, 158  
 See *O. Fischer*.
- TAUSZ.** Estimation of olefines, IX, 234
- TAYLOR.** Aconite, physiological assay of, VI, 283  
 Guaiacum test for blood, VIII, 523  
 Potassium ferrocyanide, stability of, in the presence of dilute acids, VII, 468  
 Rennet-enzyme, VIII, 126  
 Scammony resin, analyses of, VII, 134  
 See *Dixon, Woodman*.
- TAYLOR, A. SWAINE.** Poisoning by atropine and its allies, VI, 310  
 opium, VI, 434
- TAYLOR, FRANK O.** Alkaloids, volatile, IX, 480  
 Bases of vegetable origin, volatile, VI, 207  
 Opium alkaloids, VI, 353; IX, 496
- TAYLOR, LEO.** Reactions of ammonia and amines, VI, 11  
 Trimethylamine, VI, 16
- TAYLOR, T.** Microscopic examination of tea leaves, VI, 634
- TEICHMANN.** Hæmin test for blood stains, VIII, 574
- TELLE.** Estimation of salicylic acid, III, 482
- TELLOTSON.** See *Phelps*.
- TEMPANY.** See *Watts*.
- TEMPANY, H. A. and GREENHALGH, N.** Lime oil, IX, 366
- TERRAT.** See *Petit*.
- TERRY.** See *Eastes*.
- TERRY, H. L.** Percentage of resin in india-rubber, IV, 111
- TERVET.** See *Hewitt*.
- TERVET, R.** Analysis of petroleum residuum, III, 196
- TERWEN.** See *de Bloeme*.
- TESCHEMACHER and SMITH.** Assay of opium, VI, 419
- TESTONI.** Saccharin, estimation of, in foods containing benzoic acid, III, 436  
 Saccharose, estimation of, in condensed milk, IX, 56  
 See *Bignami*.
- THAL.** Correction for the filter-paper dissolved by an alkaline liquid, IV, 128
- THANNHAUSER.** See *Piloty*.
- THATCHER and KOCH.** Flour, diastase from, IX, 594
- THAYER, H. T.** Manufacture of methyl salicylate, III, 493
- THEBAULT.** Estimation of lactose in milk optically, I, 370
- THEBAULT.** See *Lefort*.
- THEBAULT, P.** Commercial bismuth salicylate, III, 489
- THIELE.** Uroferric acid, VII, 407  
**and STANGE.** Preparation of semicarbaside, IV, 235
- THIERFELDER.** Reduction of glycuronic acid, VII, 397
- THOERNER.** Constants of the mixed fatty acids from cacao butter, II, 178  
 from coconut oil, II, 188  
 palm-nut oil, II, 196  
 Linseed oil, fatty acids from, II, 337  
 rotation of, II, 338  
 Palm oil, iodine value for the mixed fatty acids from, II, 184  
 Refractive index for the fatty acids from almond oil, II, 103  
 arachis oil, II, 93  
 castor oil, II, 161  
 codliver oil, II, 215  
 linseed oil, II, 350  
 olive oil, II, 108  
 rape oil, II, 124  
 sesame oil, II, 142  
 tallow, II, 209
- THOMANN.** Detection of salicylic acid, IX, 301
- THOMAS.** Matico-camphor, IV, 210  
 See *Gawnt, White, Will*.
- THOMAS, ARTHUR W. and DAVIS, W. A.** Aliphatic acids, IX, 90
- THOMPSON.** Boric acid, estimation of, in pickle for meat curing, VIII, 371  
 Gelsemine, formula for, VII, 32  
 Hydrastine, volumetric estimation of, VI, 569  
 Linseed oil, ash from, II, 332  
 coagulation of, II, 328  
 See *Harden, Wright*.
- WALLACE and CLOTWORTHY.** Estimation of creatinine, IX, 610
- THOMPSON, C.** See *C. R. Alder Wright*.
- THOMPSON, F. A.** Gelsemine and gelseminine, separation of, VII, 34  
 Gelsemium alkaloids, extraction of, VII, 30
- THOMPSON, J.** Rosin oil, composition of, IV, 40  
 test for, IV, 43
- THOMS.** Alkaloids, estimation of, by means of Dragendorff's reagent, VI, 190  
 Cinnamic aldehyde, detection of, in oil of cinnamon, III, 444  
 Exhauster for the estimation of oils and fats, II, 5  
 Lactic acid, test for, VII, 435  
 Methyl-nonyl ketone, IV, 189  
 Onocerot, II, 488  
 Phytosterol, substances analogous to, II, 487  
**and BILTZ.** White peru balsam, III, 455
- FENDLER.** Unsaponifiable matter in linseed oil, II, 333

- THOMS, H.** Estimation of eugenol, iv, 295  
Parsley oil, iv, 369  
See *Semmler*.
- THOMSON.** See *Allen, Nordlinger*.  
and **BALLANTYNE.** Blown oils, II, 362  
Determination of the rise of temperature on the addition of sulphuric acid to fixed oils, II, 60  
Linseed oil, unsaponifiable matter in, II, 333  
Olive oil, free oleic acid in various samples of, II, 109  
Valenta test for fats and oils, II, 63
- DUNLOP.** Codliver oil, butyro-refractometer values for, II, 218  
colour tests for, II, 220  
effect of oxidation on, II, 218  
substitutes for, II, 216  
Fish-liver oils, II, 221, 223  
Linseed oil, constants of, II, 350  
iodine value for, II, 334  
refractive index of, II, 338  
unsaponifiable matter in, II, 334  
Olive oil, free oleic acid in, II, 109  
iodine value for, II, 113  
Porpoise oil, II, 231  
Seal oil, butyro-refractometer values for, II, 227
- THOMSON, R. J.** See *R. R. Tallock*.
- THOMSON, R. T.** Basicity of acids as shown by different indicators, III, 554  
Congo-red as an indicator, v, 177  
Flour, estimation of sulphates in, IX, 594  
Indicators, grouping of, III, 552  
Lacmoid, v, 344  
Turmeric as an indicator, v, 415
- THOMSON, W.** Estimation of indigo, in presence of starch, IX, 446  
Reagents for ink, for the identification of handwriting, v, 677
- THÖNY.** See *Winterstein*.
- THORBURN.** Morphine, estimation of, IX, 508
- THORBURN, A. D.** Assay of opium, VI, 429
- THORN.** Ripening of cheese, VIII, 245
- THORNE.** Purification of hydrochloric acid for use in the estimation of arsenic in malt, I, 147  
and **JEFFERS.** Estimation of starch in infants' foods, VIII, 233
- THÖRNER.** Estimation of the acidity of milk, VIII, 160
- THORPE.** Arsenic, estimation of, in hops, VII, 186  
Butter fats, examination of, II, 290  
Butters, British, Reichert-Meissl value for, II, 284  
saponification value for, II, 287  
specific gravity of, II, 286  
Driers, II, 360  
Fractional distillation, I, 20  
Linseed cake, analysis of, IX, 181  
and **HOLMES.** Alcohol, estimation of, in essences and tinctures, I, 129; IV, 102  
Methyl alcohol, estimation of, in the presence of ethyl alcohol, I, 94  
Methylated spirit, estimation of, in tinctures, I, 95, 96
- THORPE, J. F.** See *J. C. Cain*.
- THORPE, T. E.** Action of heat on tannins, v, 8  
Calculation of the original solids in decomposed samples of milk, VIII, 177  
Paraffin and waxy matter in tobacco, VI, 242
- THRESH.** Dragendorff's reagent for alkaloids, VI, 190  
Apparatus for the exhaustion of organised tissues by solvents, I, 79  
Exhauster for the estimation of oils and fats, II, 5
- THRESH, J. C.** Estimation of acetaldehyde, I, 265
- THUAU.** Chestnut-oak extracts, IX, 397  
Oak extract, IX, 397  
and **KORSAK.** Estimation of nitrogen in leather, v, 108  
Penetration of water through leather, v, III
- THUAW, W. J.** Percentage of tannin in Caledonian woods, v, 33
- THURSTON.** Detection of rosin oil in linseed oil, IX, 195
- THURSTON, R. H.** Tester for lubricating oils, III, 171
- TICKLE.** Assay of opium, VI, 428  
See *Dunstan*.
- TIDY, C. M.** Composition of creosote oil, III, 367
- TIEMANN.** Linalol, specific gravity of, IX, 341  
Milk-globulin, VIII, 131  
Vanillin, test for, III, 516  
and **HAARMANN.** Percentage of vanillin in vanilla, III, 514
- KOPPE.** Separation of phenoloid constituents in wood-tar creosote, III, 351
- KRUGER.** Ionone, IV, 190  
Purification of geraniol, IV, 259
- REIMER.** Synthesis of salicylic aldehyde, III, 500
- SCHMIDT.** Citronellal, two optically opposed modifications of, IV, 269  
Citronellol, IX, 341  
constitution of, IV, 263  
detection and estimation of, in admixture with geraniol, IV, 265  
Pulegone, synthesis of, IV, 211
- TIEMANN, F.** Citral, detection and estimation of, in essential oils, IV, 271, 272, 273  
two isomers of, IV, 267, 268  
Citronellal, commercial, IV, 269  
Geraniol, effect of heating, with strong alcoholic potash, IV, 260
- TIJDENS.** See *Van der Laan*.
- TILANUS.** Keratoids, VIII, 673
- TILDEN.** Classification of aloins, VII, 139  
Composition of cherry-laurel oil, III, 420  
See *Armstrong*.  
and **BURROWS.** Derivatives of pinene, IV, 182  
**WILLIAMSON.** Dipentene dihydrochloride, IV, 173
- TILDEN, W. A.** Isoprene, IV, 164  
*d*-pinene in anise oil, IV, 311  
Terpenes, IV, 166, 167  
Russian turpentine oil, IV, 401  
Turpentine, rotation of oil, IV, 406
- TILLMANS.** See *Olig*.



- TILLSON. Asphalt, composition of, III, 63  
 Refined, III, 60  
 Rock-asphalt composition of, III, 61
- TINKLER. See *Lander*.
- TIPLER. Palm oil, analysis of, II, 185, 186  
 Iodine value of the liquid fatty acids from, II, 184
- TOCH. Linseed oil, colour of, II, 326  
 Extraction of, from linseed, II, 325  
 Drying oils, IX, 184
- TOCH MAXIMILIAN. Soja beans, IX, 137
- TOCHER, J. P. Distillation products from various oils and hydrocarbons, III, 136
- TOCHS. Change in composition of linseed oil on oxidation, II, 346
- TOLLENS. Galactose, estimation of, by the formation of mucic acid, I, 377  
 Glycuronic acid, detection of, in the presence of pentoses, I, 400  
 Sugars, specific rotatory power of, I, 306  
 See *Maurenbrecker, Schöne*.  
 and RORIVE. Test for glycuronic acid, VII, 397
- TOLLENS, B. See *F. Mann*.
- TOLLIUS. See *Sack*.
- TOLMAN. Colour test for codliver oil, II, 220  
 Extraction of fruit colours, v, 632  
 See *Crampton*.  
 and MUNSON. Lard oil, acidity of, II, 198  
 constants for, II, 199  
 Linseed oil, composition of, II, 330  
 Olive oils and their fatty acids, iodine values of, II, 114, 115  
 oil, free oleic acid in, II, 109  
 Palm oil, iodine value for the mixed fatty acids from, II, 184  
 Poppyseed oil, iodine value for, II, 152, 153  
 solid fatty acids from, II, 152  
 Rape oil, solid fatty acids in, II, 123  
 saponification value for, II, 115  
 Sunflower oil, II, 154  
 and SMITH. Use of the Abbé refractometer in estimating sugars, I, 316
- TONKIN, R. W. Nicotine, estimation of, IX, 485  
 and tobacco, VI, 237
- TORNÖE, H. Optical determination of the alcohol and extract in beer, I, 156
- TORQUATI. Hordenine, formation of, in barley, IX, 477
- TORTELLI and PEGAMI. Molecular equivalents of insoluble fatty acids in linseed oil, II, 337  
 weight of fatty acids, II, 377
- PIAZZA. Estimation of saccharin, IX, 290
- RUGGERI. Almond oil, iodine value of liquid fatty acids from, II, 103  
 Arachidic acid from arachis oil. Estimation of, II, 98, 101  
 percentage of, isolated from arachis oil, II, 96, 97  
 Arachis oil, estimation of, II, 94  
 iodine values of, II, 92  
 Castor oil, iodine value of the mixed fatty acids from, II, 161  
 Cottonseed oil, detection of, in the fatty acids from the lead soaps, II, 138  
 estimation of mixtures containing, II, 95
- TORTELLI and RUGGERI. Hazelnut oil, iodine value of, II, 106  
 Olive oils and their fatty acids, relation between iodine values of, II, 114  
 Poppyseed oil, iodine value of the liquid fatty acids from, II, 152  
 Rape oil, iodine value of the liquid fatty acids from, II, 124  
 Sunflower oil, iodine value of the liquid fatty acids from, II, 154  
 Tallow, iodine value of the fatty acids from, II, 209  
 Walnut oil, iodine value for the mixed fatty acids from, II, 158
- TOSO. See *Paladino*.
- TÖTH. Estimation of nicotine, VI, 240; IX, 485  
 Tobacco smoke, VI, 252
- TRAGANOWSKI, P. Theobromine in cocoa, VI, 700
- TRALLES. Specific gravity of aqueous ethyl alcohol, I, 110
- TRAPS, G. S. See *A. C. Deiler*.
- TRAUB. Composition of cocoa butter, II, 177  
 and HOCK. Lacmoid, v, 344
- TRAUBE. Form of viscosimeter for oils, III, 157
- TREADWELL and KOCH. Estimation of fluorides in wines, I, 176
- TRESCOT. See *Crampton*.
- TRETZEL. See *Hilger*.
- TREUB. Formation of hydrocyanic acid in tropical plants, VII, 462
- TRIER. See *Schulze*.
- TRILLAT. Dimethylaniline test for formaldehyde, I, 259  
 Gelatin, estimation of, in gums, VIII, 592  
 Glycerol, estimation of, in wines, I, 167
- TRILLAT, A. Calcium derivative of guaiacol, III, 344  
 Estimation of glycerophosphates, II, 452
- TRILLICH and GÖCKEL. Estimation of caffeic acid, VI, 658
- TRIMBLE. Extraction of tannins, v, 3  
 Reactions of purified oak bark tannins, v, 52  
 and SCHRÖTER. Benzoic acid in wintergreen and birch oils, III, 494  
 Camphor oils, IV, 322
- TRIMBLE, H. Colorimetric determination of quinine, VI, 511
- TRÖGER and BENTIN. Pine-needle oils, IV, 382  
 and LINDE. Estimation of berberine, VI, 558
- TROG. See *Tschirch*.
- TROILI-PETERSSON and GERDA. Nature of the fat in cheese, VIII, 246
- TROTMAN and HACKFORD. Foaming of glues, VIII, 606  
 Test for glue, VIII, 613
- TROWBRIDGE and FRANCIS. Glycogen in muscle extractives, IX, 607
- TRUCHON and MARTIN-CLAUDE. Extraction of fruit colours, v, 632
- TRUCHOT, P. Specific gravity of silk and artificial silk, VIII, 669
- TRUNKEL. Composition of gelatin coagulum formed in the oxidation method of tannin assay, v, 61
- TRUNKEL, HANS. Precipitation of glue, VIII, 613



- TRÜMPLER. See *Baur*.
- TRUMMER. Estimation of lactic acid, VII, 438
- TSCHIRCH. Alban, IV, 158  
Cinchona-red, VI, 483  
Copaiba balsam, composition of, IV, 82  
Illuric acid, IV, 5, 83  
Phytosterol from grass, II, 485  
Resins, composition of, IV, 1, 2, 3  
coniferous, IV, 79  
Shellac, IV, 68  
Tea leaves, microscopic examination of, VI, 635
- and AWENG. Composition of amber, IV, 18  
Succinoabietic acid, IV, 5
- BALZER. Callitrolic and sandaracolic acids, IV, 5
- BAUR. Chironolic acid, IV, 5  
Panaxresenes, IV, 6  
Panax resinotannol, IV, 4
- BERGMANN. Herabol myrrh, IV, 98
- CONRADY. Galbanoresinotannol, IV, 4
- CREMER. Manila elemi, IV, 96
- DIETERICH, K. Dracoalban and dracore-sene, IV, 6  
Dracoresinotannol, IV, 4  
Dragon's blood resin, composition of, IV, 62
- ENGEL, A. Composition of copals, IV, 49  
Congo and Benguela copals, IV, 56
- FARNER. Aleuritic acid, IV, 5
- GERMANN. Myroxoresene, IV, 6
- GLIMMANN. Dammarresenes, IV, 6  
Dammarolic acid, IV, 5
- HALBEY. Boswellic acid, IV, 5  
Olibanoresene, IV, 6
- HILDEBRAND. Erythroresinotannol and xanthoresinotannol, IV, 4
- HOFFBAUER. Aloes, analysis of, VII, 148  
Bornträger's test for, VII, 144  
Klunge's test for, VII, 144
- HOHENADEL. Sagaresinotannol, IV, 4
- KLAVERNESS. Uganda aloes, VII, 147  
resinotannol of, IV, 4
- KNITL. Oporesinotannol, IV, 4
- LÖDY. Siarasinotannol and sumaresinotannol, IV, 14
- LUZ. Ammoresinotannol, IV, 4
- MÜLLER. Composition of alban and fluavil, IV, 158
- OBERLÄNDER. Tolu resinotannol, IV, 4
- OESTERLE. Alban, IV, 6  
Alo-emodin, VII, 150  
Fluavil, IV, 6
- PEDERSEN. Aloresinotannol, IV, 4  
Barbaloina, VII, 140  
Bornträger's test for aloes, VII, 144
- POLASEK. Asaresinotannol, IV, 4
- REUTTER. Caricari elemi, IV, 96  
Mastic, composition of, IV, 59  
Masticic, masticolic and masticonic acids, IV, 5  
Masticoresenes, IV, 6
- SAAL. Carana and colophonia elemi, IV, 96
- STEPHAN. Copal resenes, IV, 6  
Trachylolic acids, IV, 5  
Zanzibar copal, composition of, IV, 49
- TSCHIRCH and, STUDER. Formula of abietic acid, IV, 22
- TROG. Peru resinotannol, IV, 4
- WEIL. Gurjun resene, IV, 6
- WOLFF, M. Composition of sandarac, IV, 57
- TSCHOUGAEF, L. A. Separation of borneol and isoborneol, IV, 279
- TSUJIMOTO. Acid in whale oil, II, 229  
Iodine value of Japanese sardine oil, II, 224  
Sardine oils, II, 225
- TUCHOLKA. Bisabol myrrh, IV, 98  
test for, IV, 100  
Oil of myrrh, IV, 103
- TUCKER, D. L. Determination of the acidity in hide powder, V, 81
- TUFTS. See *Gill*.
- TUNMANN. Alkaloids, detection and estimation of, IX, 479  
in nux vomica seeds, IX, 478  
Azeca alkaloids, IX, 480  
Cinnamic acid, detection of, IX, 292
- TURNER. Test for gurjun balsam, IV, 88
- TURNER, J. L. and VANDERKLEED, C. E. Estimation of acetanilide and phenacetin, VI, 103
- TUTIN. Dextrose phenylosazone, melting point of, I, 373  
Hyoscine, constitution of, IX, 490  
Quinine sulphate, Kerner test for, VI, 521  
specific rotation of, VI, 517  
titration of, VI, 496  
Scopoline, VI, 294  
See *Barrowcliff*.
- and CLEWER. Constitution of chrysophanic acid, V, 227  
Solangustine, IX, 546
- HANN. Glycerylphosphoric acid, II, 453
- TUTIN, F. See *F. B. Power*.
- TUTTLE. See *Waters*.
- TUTTLE, J. B. Printing inks, IX, 456  
and SMITH, W. H. Analysis of printing inks, IX, 457, 458  
See *W. H. Smith*.
- TUTTON. Crystallographic characters of aconitine, VI, 259
- TUTWEILER, C. C. Coal-tar, typical analyses of, III, 27  
Drip oils, testing of, IX, 261  
Water-gas tar, analyses of, III, 34
- TWADDELL. Hydrometer of, I, 7
- TWITCHELL. Fat splitting enzymes, VIII, 292  
Petroleum, use of, in Muter's estimation of fatty acids, II, 392  
Rosin and fatty acids, separation of, II, 77  
Saturated and unsaturated fatty acids, separation of, by means of sulphuric acid, II, 392
- TYRER and WERTHEIMER. Terebene, IV, 427

## U

- UBBELOHDE. Determination of the melting point of lubricating greases, III, 175  
See *Engler, Holde*.

- UDRANSKY. Bile acids, detection of, IX, 579  
 See *Baumann*.  
 and BAUMANN. Putrescine, VII, 347
- UFFELMANN. Detection of lactic acid in gastric juice, VII, 435  
 and BÖMER. Composition of kola, VI, 681
- UHLENHUTH. Testing for horseflesh, VIII, 273
- UHLIK. Preservation of small quantities of oxy-hæmoglobin, VIII, 510
- UHLIRZ. See *Landsteiner*.
- ULEX, G. L. Detection of ethyl alcohol in fusel oil, I, 130
- ULPIANI, C. and PAROZZANI, A. Analysis of citric acid, IX, 112
- ULRICH. Formula of columbin, VI, 576
- ULZER. Composition of coconut oil, II, 188  
 See *Benedikt*.  
 and DEFRIS. Shellac resin acids, IV, 69  
 ZUMPFER. Grape seed oil, II, 175
- ULZER, F. and SEIDEL, H. Lactic acid, estimation of, VII, 440, 443  
 Wool-fat, total acidity number of, II, 501
- UMBER.  $\alpha$ -Nucleoprotein, VIII, 92
- UMNEY. Aniseed oil, IX, 351  
 Cinnamon oil, detection of adulteration of, III, 444  
 Japanese and other peppermint oils, distinction between, IX, 372  
 Otto of rose, analyses of, IX, 330  
 Rose oil, IV, 387  
 Storax, liquid, analysis of, IX, 297  
 and BENNETT. Chinese neroli oil, IV, 368  
 Cinnamon oil, specific gravity of, IX, 356  
 Copaiba balsam, official requirements for, IV, 86  
 origin of, IV, 82  
 Pennyroyal oil, IV, 377  
 Sicilian peppermint oils, IV, 371  
 South American orange oil, IV, 364
- POTTER. Oil of cubebs, IX, 358
- SWINTON. Composition of commercial citronella oils, IV, 305  
 Geranyl acetate in lemon oil, IV, 353
- UMNEY, J. C. Almond oil, acidity of, IX, 130  
 Anise oil, melting point of, IV, 312  
 Asafoetida, tincture of, IV, 95  
 Caraway oil, specific gravity of, IV, 324  
 Cativo balsam, IV, 90  
 Copaiba oil, varieties of, IV, 85  
 Dill oil, differences in, according to origin, IV, 335  
 Eugenol, estimation of, in oil of cloves, IV, 294  
 Lavender oils, specific gravity of, IV, 347  
 Peppermint oils, IV, 371  
 Petroleum in anise oils, IV, 313  
 Star-anise oils, IV, 313
- URBAIN. Composition of cutose, I, 435
- U. S. DEPT. AGRICULTURE. Abrastol, tests for, III, 259  
 Butter, foam test for, II, 299  
 Cereals, analyses of, VIII, 108  
 Citric acid, estimation of, in fruit juices, I, 563  
 Creosote and cresylic acid sheep dips, analysis of, III, 318  
 oils, specifications for, III, 369
- U. S. DEPT. AGRICULTURE. Inks, V, 671  
 Meat foods, estimation of ammonia in, IX, 612  
 $\beta$ -Naphthol, detection of, in foods, III, 257  
 Olive oil, II, 112  
 Potable spirits, estimation of aldehydes in, I, 198  
 higher alcohols in, I, 196  
 Salicylic acid, influence of, on digestion, III, 469  
 Typewriter ribbons, testing of, V, 687  
 Vinegar, commercial, analysis of, I, 504  
 See *Bigelow*.
- URTZ. Blood, phenolphthalein test for, VIII, 525  
 Cheese, analysis of, IX, 600  
 Codliver oil, butyro-refractometer values for, II, 218  
 Cottonseed oil, test for, IX, 135  
 Essential oils, refractive index of, IV, 245  
 Gurjun balsam, detection of, IV, 89  
 India-rubber, estimation of, IX, 321  
 Lactic acid, separation of, VII, 436  
 Milks, dried, analysis of, IX, 600  
 Poppyseed oil, commercial, sesame oil in, II, 152  
 rotation of, II, 153  
 Salicylic acid, occurrence of, in fruit, III, 466  
 Segura balsam in copaiba balsam, IV, 82  
 Sesame oils, comparison of varieties of, II, 143
- V
- VAMVAKAS. Detection of saponin in beverages, VII, 129
- VALENTA. Composition of bone fat, II, 205  
 Chinese vegetable tallow, II, 181  
 Palm-nut oil, II, 195  
 Test for oils and fats, based on their solubility in glacial acetic acid, II, 62  
 and FEIGERLE. Detection and estimation of rosin oil in mineral oils, IV, 45
- VALENTA, E. Combining weights of the fatty acids, II, 380  
 Influence of carnaúba wax on the melting point of mixtures containing it, II, 272
- VALENTE. See *Carnelutti*.
- VALENTI. Meconic acid, VI, 412
- VALENTIN, W. G. Analyses of commercial starch sugars, I, 379
- VALEUR. Genisteine, IX, 483  
 See *Mourou*.
- VALSER. See *Grandval*.
- VANDERKLEED. Digitalis glucosides, estimation of, VII, 120  
 See *E'we*.
- VANDERKLEED, CHARLES E. Strychnos alkaloids, VI, 441; IX, 510  
 See *J. L. Turner*.
- VANDEVELDE. Compounds which retard rennet coagulation, VIII, 130
- VANICEK, R. Estimation of tannic acid, IX, 404
- VASEY. Analysis of potable spirits, I, 199  
 See *Heaton*.
- VAUBEL. India rubber, estimation of, IX, 321  
 naphthylamine sulphonc acids, analysis of, VI, 124

- VAUBEL.** Oils, bromine values of, IX, 189  
 Shellac, bromine absorption of, IX, 312  
**VAUGHAN.** Tyrotoxon, VII, 355  
**VEDDER.** Ipecacuanha alkaloids, IX, 541  
**VEIT, T.** See *J. Paessler*.  
**VEITCH and DONK.** Wood turpentine, IX, 381  
**VEITCH, WILSON, J.** Effect of temperature on the viscosity of lubricating oils, III, 147  
**VEITSCH.** Analysis of leather, V, 109  
**VELEY.** Estimation of higher alcohols in potable spirits, I, 192, 194  
 Quinine and cinchona alkaloids as diacidic bases, VI, 202  
 and **WALTER.** Toxicity of theobromine and of caffeine, VI, 592  
**VENABLE, F. P.** Composition of the leaves of the yopon, VI, 642  
**VENTURINI.** Kieffer's process for the estimation of morphine, VI, 385  
**VERLEY and BÖLSING.** Estimation of free eugenol in essential oils, IV, 296  
**VERNON.** Indophenol test for oxydases, VIII, 13  
**VESTERBERG.**  $\alpha$ -Amyrol, II, 488  
**VESTERBERG, A.** Pimaric acid, IV, 22  
**VICARIO, A.** Vaseline oil, IX, 259  
**VICTOR.** Estimation of cyanates, VII, 541  
**VIERHONT.** Estimation of salicylic acid, IX, 302  
**VIETH.** Butter analyses of, II, 306  
 Buttermilk, analysis of, VIII, 196  
 Cheese estimations of fat and total solids in, VIII, 252  
 Koumiss, analysis of, VIII, 230  
 Kerosene, refined, turbidity in, III, 135  
 Milk, analysis of, VIII, 141  
 Dried, analysis of, VIII, 238  
 Skim, composition of, VIII, 186  
 and **RICHMOND.** Analysis of clotted cream, VIII, 186  
**VIGNON.** Fibroin, pure, preparation of, VIII, 636  
 Gallic acid, absorption of by ungummed silk, III, 528  
 Silk, determination of the weighting of, VIII, 654  
 See *Dubois*.  
 and **SILBERMANN.** Specific gravity of textile fibres, VIII, 654  
**SISLEY.** Nitro silk, VIII, 638  
**VIGNON, L.** Estimation of tannin, V, 93  
 Optical activity of silk solutions, VIII, 640  
**VILLAVECHIA and FABRIS.** Olive oils, furaldehyde test for, II, 145  
 Sesame oil, II, 142  
 Furfuraldehyde, test for, II, 144  
 Phytosterol from, II, 486  
**VILLE, J.** Anhydrous quinine, IX, 516  
**VILLIERS.** Detection of saccharin in foods and beverages, III, 432  
 and **COLLIN.** Microscopical examination of pepper and its adulterants, VII, 59  
**VILLIGER.** See *Baeyer*.  
**VILLON, M.** Estimation of tannin, V, 88  
**VINASSA.** Testing of saffron, V, 420  
**VIRCHOW.** Estimation of caffeine in coffee, VI, 609  
**VIRCHOW, C.** Effect of feeding animals with phytosterol, II, 489  
**VISHI, H.** Manufacture of camphor oil, IV, 320  
**DE VISSER, L. E. O.** Solidifying points of mixtures of stearic and palmitic acids, II, 386  
**VITALI.** Abrastol, tests for, III, 401  
 Chloroform, estimation of, I, 275  
 Hydrastine, test for, VI, 567  
 Salicylic acid, detection of in preserved tomatoes, III, 479  
 use of toluene in the extraction of, III, 477  
 and **STROPPA.** Odour of coniine, VI, 212  
**VITALI, D.** Detection of acetylene in cases of poisoning, III, 10  
 Test for atropine, VI, 306  
**VAN VLOTEN, H. K.** Formogelatin, VIII, 601  
**VÖLCKER.** Estimation of hippuric acid in urine, VII, 394  
**VOELCKER.** Analysis of English cheddar cheese, VIII, 251  
**VOELLER, F.** Estimation of indigotin, V, 402  
**VOGEL.** Detection of other flours in wheaten flour, I, 461  
 Fungus in flour, I, 458  
**VOGEL, A.** Test for quinine, VI, 511  
**VOGT.** See *Windschütz*.  
**VOIGTLÄNDER.** Iodine value for lard, II, 318  
**VOISENET.** Detection of methyl alcohol, I, 90  
**VOLEY-BOUCHER.** Enzyme in gums, I, 439  
**VOLHARD.** Preparation of potassium cyanate, VII, 537  
**VOLHASE.** Benzoic acid, detection of, in fats, IX, 282  
 Saccharin, detection of, IX, 289  
**VONDRAČEK.** See *Votoček*.  
**VONGERICHTE, E.** Detection of pyridine, VI, 136  
**VOORHEES.** Manganese in linseed oil ash, IX, 187  
 See *Osborne*.  
**VORTMANN.** See *Messinger*.  
**VOTNMESSIL.** See *Votoček*.  
**VOTOČEK and VONDRAČEK.** Decomposition products of solanine, VII, 90  
 and **VOTMESSIL.** Detection of carbon disulphide in commercial benzols and naphthols, III, 226  
**VOURNASOS.** Detection of lactic acid, VII, 435  
**DE VRIES.** See *Boekhout*.  
**DE VRIJ, J. E.** Estimation of quinine, VI, 513  
 the total alkaloids in cinchona bark, VI, 489  
**DE VRY.** Cinchona alkaloids, separation of, VI, 491  
 Quinidine, cinchonidine and amorphous alkaloids, distinction between, VI, 545  
 Quinidine sulphate, detection of other alkaloids in, VI, 535  
 Quinine chromate, solubility of neutral, VI, 514  
 sulphate, commercial, detection of other alkaloids in, VI, 522, 527  
**VUAFLART, L.** Poppseed oil, IX, 139  
**VULPIS, G.** Assay of diuretin, VI, 594  
**VULTÉ and GIBSON.** Reichert value for maize oil, II, 140  
 and **LOGAN.** Bromine and iodine values for fats and oils, II, 27

## W

- WACHHOLDER. See *Schöndorff*.
- WACKER, LEONHARD. Sterol substance in human fat, IX, 227
- WACKERNAGEL and WOLFFENSTEIN. Sparteine, VI, 232, 234
- WADE. See *Smith*.
- and PANTING. Preparation of hydrocyanic acid, VII, 464
- DE WAELE. Estimation of rosin in linseed oil, IX, 200
- Separation of fatty acids in oils and fats, IX, 185
- VAN DER WAERDEN. See *Van Gijn*.
- WAGENAAR. Identification of purine derivatives, IX, 525
- WAGER. See *Dangeard*.
- WAGNER. Alcohol, estimation of, by means of the refractometer, I, 126
- Antimony, estimation of, in vulcanised rubber, IV, 143
- Yeast, chemical composition of, I, 208
- See *Sprinkmeyer*.
- and BRYKNER. Bornylene, IV, 183
- RINCH. Estimation of sugar by the formation of cupric nitrate, I, 335
- WAHLGREN. Isolation of glycocholeic acid from ox-bile, VIII, 412
- WAINWRIGHT, J. H. Distinction between crude and distilled glycerin, II, 476
- WALBUM. Detection of turpentine in Venice turpentine, IV, 79
- See *Bertram*.
- and HÜTHIG. Composition of oil of cinnamon, III, 443
- WALBUM, L. E. Detection of colophony in copaiba balsam, IV, 90
- WALDEN. Gallotannic acid, IX, 385
- See *Lauder*.
- WALDEN, P. Molecular weight of gall-tannin, V, 17
- WALDER. See *Abderhalden, Gnehn, Grandmougin*.
- WALKER. Casein, estimation of, in milk, IX, 596
- Linseed oil, Foot's test for, IX, 186
- Potassium ferricyanide, preparation of, VII, 524
- See *Bennett, Munson*.
- and HAMBLY. Transformation of urea to ammonium cyanate, VII, 290
- JOHNSON. Tetralkyl ammonium bases, VI, 21
- WARBURTON. Candle nut oil, brominated glycerides from, II, 149
- Oils, insoluble, bromide values for, II, 29
- Sardine oils, II, 225
- Sperm oil, insoluble brominated esters from, II, 239
- Tung oil, action of bromine on, II, 155
- Whale oil, composition of, II, 229
- WEISS. Rideal-Walker phenol control, IX, 277
- WALKER, J. and BLACKADDER, J. Estimation of carbon and hydrogen by combustion, I, 58
- WALKER, PERCY H. Inks, V, 669; IX, 468
- WALKOFF. Estimation in commercial cane sugar of organic matters not sugar, I, 350
- WALLACE. Adulteration of ground coffee, VI, 670
- Solubility of potassium ferricyanide, VII, 525
- See *Levene, Richardson, Thompson*.
- WALLACE, W. Analysis of ash from Demerara cane sugar, I, 345
- WALLACH. Fenchene, IV, 184; IX, 325
- Fenchone, IV, 211
- $\alpha$ -Limonene in sweet orange oil, IV, 359
- Nitrosochlorides of terpenes, IV, 167
- Phellandrene, isomerides of, IV, 177
- Pinene hydrochloride, melting point of, IV, 181
- Terpenes, IV, 166
- Terpineol, IX, 343
- preparation of, IV, 280
- and GROSSE. Sesquiterpene in pine-needle oil, IV, 382
- OTTO. Synthetic isomer of quinine, VI, 503
- WALLENSTEIN and PINCK. Iodine values of fats and oils and their fatty acids, II, 392
- of the liquid fatty acids from lard, II, 319
- from rape oil, II, 124
- from tallow, II, 209
- WALLER. Estimation of hydrocyanic acid in vegetable and animal tissues, VII, 470
- See *Veley*.
- WALLERSTEIN. Phytosterol from barley, II, 485
- WALPOLE. See *Barger*.
- WALTER. Cedrol, IV, 326
- Ichthulin, VIII, 92
- Nitrocellulose, detection of, in artificial silk, VIII, 667
- WALTER, J. Colour change in moist phenol, III, 293
- WALTHER. Estimation of citral in essential oils, IV, 276
- WALTHER, J. Estimation of carvone, IV, 216
- WALTON, W. See *F. W. Richardson*.
- WANKLYN. Fractional distillation, I, 19
- VAN DER WANT. See *Geitel*.
- WARBURTON. See *Walker*.
- WARD. Guaiacum, IV, 65
- See *Brown*.
- WARD, MARSHALL. Culture yeast, I, 215
- WARDEN and BOSE. Analyses of canned meats, VIII, 333
- WARDEN, C. J. H. Cocatannic acid in coca leaves, VI, 344, 345
- WARDLE. Appearance of different varieties of silk, VIII, 641
- and BELL, CARTER. Silk, weighting, VIII, 653
- WARDLEWORTH, T. H. Spurious ipecacuanhas, VII, 49
- WARE and SCHUMANN. Adulteration of tung oils, IX, 143
- WARINGTON. Citric acid, loss of acidity of juices by concentration, I, 559
- Potassium hydrogen tartrate, table showing the effect of some acids and salts on the solubility of, I, 552
- Tartaric acid liquors, estimation of total organic acids in, I, 542
- test for lead in commercial, IX, 101

- WARREN.** Fractional distillation, I, 20  
 Specific gravity of benzene, III, 203  
 and **STORER.** Rangoon tar, III, 44  
**WEISS.** Picrolonic acid as a reagent for alkaloids, VI, 187  
**WARREN, BRUCE.** The analysis of oils by their interaction with sulphur chloride, II, 40  
**WARTENBURG.** See *Connstein*.  
**WASOWICZ.** Reactions of atisine, VI, 278  
**WATERMAN.** Distinction between the whites of hen and duck eggs, IX, 621  
 See *Boesken*.  
**WATERS and TUTTLE.** Estimation of sulphur in rubber, IX, 323  
**WATSON, G. N.** Test for cinchona alkaloids, IX, 515  
**WATSON, H. J.** Glue, VIII, 602, 606  
**WATTS and TEMpany.** Method of clarifying sugar solutions, I, 310  
 Use of citric acid for the inversion of sugar in milk, I, 370  
**WAUTERS.** Detection of coconut fat in cacao butter, VI, 718  
 Furfuraldehyde test for sesame oil, II, 144  
**WAY and OGSTON.** Ash of various roots, VI, 655  
**WEBER.** Ebonite, analysis of, IV, 144  
 India-rubber, acetone extraction of, IV, 123, 124, 125, 126  
 analysis of, IV, 110, 112  
 hydrocarbon of, IV, 107  
 latex, transformation of, into india-rubber, IV, 105  
 percentage of resin in, IV, 111  
 vulcanisation of, IV, 115, 116  
 vulcanised, analysis of, IV, 131  
 substitute in, IV, 129  
 tests for, IV, 118  
 See *Poleck*.  
**WEBSTER.** See *Gane, Nierenstein*.  
 and **PURSEL.** Estimation of the alkaloids in nux vomica, VI, 472  
**WEGER.** Driers for oils, II, 359, 360  
 Drying of oils, effect of external influences on the, II, 347  
 Linseed oil, refractive index of, II, 338  
**WEGER, MAX.** Valuation of resinate driers, IV, 35  
**WHMAER.** Proteolytic enzyme in yeast, I, 212  
**WEIGEND.** See *Beilstein*.  
**WEIGEL, G.** Optical activity of oil of copaiba, IV, 85  
**WEIGELIN.** Alkaloids of sabadilla, VII, 70  
**WEIGNER.** Serum of milk obtained by precipitation of the curd, VIII, 197  
**WEIL.** Alternative formula for carbinol bases, V, 236  
 See *Abderhalden, Tschirch*.  
**WEIL, H.** Homolka's base, V, 235  
 See *P. Landauer*.  
**WEIN.** Table for the estimation of maltose, I, 363  
**WEIN, A.** Estimation of naphthalene in coal gas, IX, 267  
**WEINGÄRTNER, E.** Colouring matters, artificial, classification of, V, 443  
 basic, examination of, V, 470  
 detection of, from meat products, VIII, 383  
**WEINSCHENK.** Use of polarising microscope, I, 41  
**WEINTRAUB.** See *Lunge*.  
**WEINWURM.** Detection of paraffin or rosin in beeswax, II, 257  
**WEISBERG.** Presence of lactic acid in molasses, VII, 429  
**WEISER and DONATH.** Iodine values for fatty acids, IX, 120  
**WEISKE.** Precipitation of tannic acid, V, 60  
 Use of salicylic acid in alkalimetry, III, 476  
**WEISKE, H.** Peptones, VIII, 396  
**WEISS.** See *Walker, Warren*.  
**WEISS, J. M.** Phenol, estimation of, IX, 270  
 Naphthalene, crude, III, 249  
**WEISWEILLER.** See *Bertrand*.  
**WEITH.** See *Redman*.  
**WEITZEL.** Compounds which retard rennet coagulation, VIII, 130  
**WEIZMANN.** Preparation of artificial camphor, IV, 192  
**WELCH and CHAPMAN.** Precipitin method for the identification of species of meat, VIII, 275  
**WELLENSTEIN.** See *Medicus*.  
**WELLER, A.** Test for quinine, VI, 510  
**WELLER and RIEGEL.** Use of the hæmoglobin of pig's blood in colouring sausages, VIII, 381  
**WELMANS.** Estimation of dextrin in chocolate, VI, 712  
**WELMANS, P.** Colour tests for peppermint oil, IV, 375  
**WELSCH.** See *Windows*.  
**WENDE.** Detection of halogens in benzoic acid, IX, 279  
**WENDEL.** See *F. Ehrlich*.  
**WENDT.**  $\alpha$ - and  $\beta$ -Methylnaphthalenes, III, 251  
**WENGLEIN.** Polarimetric estimation of starch, I, 424  
**WENTZEL, F.** See *F. Kehrman*.  
**WEPPEN, H.** Test for morphine, VI, 381  
**WERDER.** Estimation of fatty alcohols and hydrocarbons in beeswax, II, 258  
**WERDER, J.** Examination of beeswax with the butyro-refractometer, II, 249  
**WERIGO.** Formation of cadaverine in the pancreas, VII, 348  
**WERNER.** See *Berthelot*.  
**WERNER, E.** Action of bromine on salicylic acid, III, 480  
**WERTHEIMER.** See *Tyler*.  
**WERTHER.** Detection of hydrogen peroxide in milk, VIII, 173  
**WEST.** Detection of Prussian blue in tea, IX, 530  
**WEST, R.** See *G. B. Frankforter*.  
**WEST-KNIGHTS, J.** Apparatus for the exhaustion of organised tissues by solvents, I, 78  
 Exhauster for the estimation of oils and fats in very small quantities of material, II, 5  
**WESTPHAL, C.** See *O. Schumm*.  
**WETHERILL, C. M.** Coefficients of expansion of oils, II, 50  
**WETZEL.** Conchiolin, VIII, 91  
**WEYL.** Composition of silk-fibroin, VIII, 637  
 Poisoning by Martius' yellow, V, 126

- WEYL, T. Test for creatinine, VII, 314
- WHIPPEN, W. G. Homoquinine, VI, 550
- WHIPPLE. See *Jones*.
- WHITAKER, T. Nitrosophenol in picric acid, III, 585
- WHITBY. Estimation of gold in cyanide solutions, VII, 494  
See *Cripps*.
- WHITE. See *Langmuir*.  
and AVERY. Acid produced in the fermentation of milks, VIII, 224
- BALL. Estimation of naphthalene in spent oxide, IX, 268
- BRAITHWAITE. Melting point of cocoa fat, VI, 701
- THOMAS. Refractive index of China wood oil, IX, 192
- WHITE, J. Caper tea, VI, 638
- WHITE, T. P. Action of tin on the animal organism, VIII, 339
- WHITELEY. Wool-keratin, VIII, 684
- WHITFIELD. See *Pickles*.
- WHITLEY. See *Moore*.
- WHITNEY. Guaiacum test for blood, VIII, 523
- WHITTERIDGE. See *Chapman*.
- WHYMPER. See *Caldwell*.
- WHYMPER, R. Cocoa and chocolate, VI, 685
- WICHELHAUS. Structure of cachou de Laval, V, 375
- WICHMANN. Detection of coumarin in vanilla, IX, 306  
Milk-albumin, VIII, 131
- WIECHMANN. Examination of liquid sugar products, I, 334
- WIECHMANN, F. G. Use of acetic acid in clarifying beet-sugar solutions with lead acetate, I, 312
- WIECHOWSKI. Estimation of hippuric acid, VII, 395
- WIEGAND. See *Beilstein*.
- WIELAND. Estimation of creatine and creatinine, IX, 610
- VAN DER WIELEN. Opium, assay of, IX, 506  
Estimation of codeine and narcotine in, VI, 393
- WIENER. Globulins, VIII, 91  
Separation of globulin and albumin in serum, VIII, 66, 483
- WIGGERS. Preparation of pure potassium cyanide, VII, 473
- WIGNER, G. W. Tea, analyses of, VI, 604  
Extract from, VI, 622  
Moisture in, VI, 603  
Sodium chloride in, VI, 605  
Tin in canned meats, VIII, 338
- WIJS. Hübl's process for the determination of the iodine value of fats and oils, II, 31
- Linseed, foreign seed in, II, 323  
Oil, constants of, II, 350  
specific gravity of, II, 331  
Macassar oil, unsaponifiable matter in, II, 194  
Sesame oils, iodine values of, II, 143
- WIJSMAN and REIJST. Detection of coconut oil in butter fat, II, 284
- WILBERT, M. I. Asafetida, IV, 94
- WILEY. Alcohol, estimation of, in a liquid by the boiling point method, I, 126  
Lactose, removal of protein matters from milk for the optical estimation of, I, 368  
Lard, American, grades of, II, 317  
free acid in, II, 319  
Meat, composition of, VIII, 262  
Nitrogen, estimation of in pickle for meat curing, VIII, 368  
Oils and fats, modifications of the bromine thermal process for, II, 61  
Starch sugar, determination of dextrose, maltose and dextrin in, I, 381  
and EWELL. Polarimetric estimation of milk, I, 369; VIII, 159
- PENNINGTON. Detection of the decomposition of meat by microscopic examination, VIII, 312
- WILEY, H. W. Effect of benzoic acid and benzoates in food, III, 405  
Use of acetylene in polarimetric work, I, 42
- WILGERODT. See *Claus*.
- WILHELM and MEISTER. Iodine value for oxidised linseed oil, IX, 189
- WILHELM, F. Extraction of hydrastine, VI, 565
- WILHELM, P. Estimation of tannins, V, 94
- WILKIE. Phenols, estimation of, in essential oils, IX, 327  
Salicylic acid, estimation of, IX, 301  
test for, IX, 300
- WILKIE, J. M. Lead, detection of, I, 568; IX, 102  
 $\beta$ -Naphthol, estimation of, IX, 269
- WILKINSON. See *Bennett*.  
and PETERS. Detection of heated milk, VIII, 168
- WILL. Explosives, test for, III, 615  
Hydrastine, VI, 564  
Yeast, cell wall of, I, 206, 207  
Culture, I, 215  
Proteolytic enzyme in, I, 212  
Vitality of, I, 210  
See *Freund, Lindner, Neumann, Reimer*.  
and CASAGRANDE. Cell wall of yeast, I, 206
- WILL, R. See *F. Härtel*.
- WILL, WATSON. Roasting of coffee, VI, 649
- WILLCOCK and HOPKINS. Hydrolysis products of Zein, VIII, 107
- WILLIAMS. Belladonna, alkaloid in, VI, 313  
Codeine sulphate, estimation of, IX, 500  
Copals, acid value of, IV, 55  
Essential oils, iodine value of, IV, 239, 240  
Fats and oils, bromine values of, II, 27, 28  
Fish, analyses of, IX, 621  
Gold extraction, use of cyanogen bromide in, VII, 461  
Linseed oil, change of composition of, on boiling, II, 346  
composition of, II, 329  
mean molecular weight of the fatty acids from, II, 350  
specific gravity and iodine value of, II, 336  
unsaponifiable matter in, II, 333  
Morphine, estimation of, IX, 507  
sulphate, IX, 497



- WILLIAMS. Sperm oil, fatty acids from, II, 235  
and DREAPER. Estimation of Prussian blue in weighted silk, VIII, 659
- WILLIAMS, C. G. Estimation of benzene, III, 206
- WILLIAMS, GREVILLE. Preparation of pyridine bases, VI, 130
- WILLIAMS, H. E. Estimation of cyanogen in spent gas purifying mass, VII, 522  
Carbonyl ferrocyanides, IX, 588
- WILLIAMS, J. Acid impurities in salicylic acid, III, 471  
Preparation of urea, VII, 289
- WILLIAMS, JOHN. Commercial cocaine hydrochloride, VI, 329
- WILLIAMS, J. H. See *C. F. Mabery*.
- WILLIAMS, K. I. Analyses of cooked fish, VIII, 458
- WILLIAMS, R. Amber, analysis of, IV, 20  
Aniline salt, examination of, VI, 60  
Colophony, acid values for, IV, 26  
Dragon's blood resin, IV, 64  
Mastic, IV, 60  
Resins, constants for, IV, 10, 12, 13  
Sandarac, IV, 58
- WILLIAMS, R. H. Formaldehyde, estimation of, I, 260, 261
- WILLIAMSON. Alkaloids in hops, VII, 172  
See *Tilden*.
- WILLNER. Copals, IX, 310
- WILLS and HAWK. Gastric juices, IX, 581
- WILLSTÄTTER. Alkaloids, nomenclature of, VI, 170  
Aniline black, constitution of, V, 316  
Chlorophyll, V, 638  
Hyoscine, constitution of, IX, 490  
Polymethylenes, hydrogenation of, IX, 237  
Tropitidene, formula of, VI, 204  
and DOROGI. Constitution of aniline black, V, 316
- FOURNEAU. Anhydrolupinine, VI, 227  
Lupinidine, VI, 227  
Lupinine, VI, 226
- MADINAVEITIA. Estimation of glycerol in fats, IX, 222
- MARK. Lupinidine, VI, 227  
Spartyrine and oxysparteine, VI, 234
- WILLSTÄTTER, R. and BRUCE, J. Cycloparaffins, IX, 236
- WILSON. Japanese wood oil, IX, 144  
Nitrogen of fish muscle, IX, 621  
Nitrogenous muscle-extractives, IX, 609  
Turkey red oil, detection of adulterants in, II, 171  
estimation of the total alkali in, II, 171  
free acid in, II, 169  
specific gravity of, II, 168  
See *Dreaper*.
- and HEAVEN. Oxygen absorption of drying oils, IX, 193
- WILSON, G. Turpentine oil, rotation of, IV, 406  
Turpentine oil, specific gravity of, IV, 408
- WILSON, J. A. Estimation of fatty acids in soap, II, 433
- WIMMER. See *Mecke*.
- WINCKLER. Melting point of cubeb camphor, IV, 333
- WINDAUS. Cholestenone, preparation of, II, 482  
Cholesterol, estimation of, IX, 224  
and phytosterol, separation of, II, 492  
Digitonin test for, VII, 118  
Digitonin-cholesteride, preparation of, II, 481  
and HAUTH. Phytosterol from calabar bean, II, 486  
Phytosterols, II, 487  
Stigmasterol, II, 488
- HERMANN. Ipecacuanha alkaloids, constitution of, IX, 544
- SCHNECHENBURGER. Gitonin, IX, 547
- VOGT.  $\beta$ -Iminazo lylethylamine, VII, 349
- WELSCH. Brani casterol, II, 488  
Crystalline substance from the resin of *Antiaris toxicaria*, VII, 124  
Phytosterol from rape oil, II, 486, 494
- WINDISCH. Carbon dioxide, estimation of in beer, I, 157  
Glycerol, estimation of in wines, I, 167  
Lactic acid, detection of, VII, 434  
Potable spirits, analyses of, I, 200  
Salicylic acid, occurrence of in fruit, III, 466  
Wines, analysis of, I, 165  
Differentiation of malic, tartaric and succinic acids in, I, 187  
Estimation of acid in, I, 170  
sulphurous acid in, I, 174  
tartaric acid and tartrates in, I, 177  
See *Stutzer*.
- WINFIELD. Specific gravity of the mixed fatty acids from maize oil, II, 141
- WINGE, O. and JENSEN, J. P. H. Hops, determination of resins in, IX, 558
- WINGHAM, A. Ash of English tobacco, VI, 243
- WINKELBLECH, K. Determination of the temperature of gelatinisation of glue, VIII, 611
- WINKLER. Iodine value of fatty acids, IX, 120
- WINMILL. Phenosafranine, V, 322
- WINOGRADOFF. See *Meigen*.
- WINTERFELD, G. See *J. Marcusson*.  
See *Holdt*.
- WINTERS. See *Engelhardt*.
- WINTERSTEIN. Cystine, precipitation of, by phosphotungstic acid from the hydrolysis products of proteins, VIII, 83  
Morphine, isolation of from animal matter, VI, 438  
See *Schulze*.
- and KÜNG. Formation of *p*-hydroxyphenylethylamine in Emmenthaler cheese, VII, 346
- THÖNY. Cheese, formation of cadaverine in, VII, 348  
Putrescine in, VII, 348
- WINTGEN. Distinction between yeast and meat extract, VIII, 416, 417  
Formation of solanine in potatoes, VII, 93
- WINTHER. See *Schlichting*.
- WINTON. Colouring matters, detection of, V, 659; VIII, 382, 383  
Pepper, ground, adulteration of, VII, 58



- WINTON. Vinegars, estimation of the lead number of, IX, 96  
 Albright and Berry. Analyses of vanilla, IX, 307  
 and BAILEY. Separation of vanillin and coumarin, III, 520  
 Kreider. Determination of the extent of adulteration of maple products, I, 389
- WINTON, OGDEN and MITCHELL. Analysis of pepper, VII, 60  
 and SILVERMANN. Separation of vanillin and coumarin, III, 519, 520
- WIRTHLE. Detection of saccharin in foods and beverages, III, 433
- WISDON. Tannin substitutes, IX, 408
- WISHART, G. J. Tin in canned fruit, VIII, 338
- WISLICHENUS. Azoimide, preparation of, VI, 27  
 Hide powder, substitute for, v, 95  
 Phthalide, synthesis of, III, 507
- WITT. Action of reducing agents on azo dyes, v, 204  
 Detection of colouring matters from meat products, VIII, 383  
 Preparation of  $\alpha$ -naphthylamine, VI, 112  
 and THOMAS. Production of indulines, v, 326
- WITT, O. N. Production of eurhodines, v, 320  
 Tables for the identification of colouring matters, v, 447
- WITTMANN. Formula for solanine, VII, 90  
 See *Zeisel*.
- WITZECK. Estimation of cyanogen in spent gas purifying mass, VII, 521
- WOEHLER. Preparation of zinc cyanide, VII, 476  
 See *Liebig*.
- WÖHLER. Estimation of cyanates, VII, 540
- WÖHLK. Pyridine, detection of, IX, 475
- WÖLFING. Preparation of pure *p*-toluidine, VI, 68
- WOHL and NEUBERG. Glycerose, II, 452
- WOHLGEMUTH. Determination of the diastatic power of enzymes, VIII, 5  
 Liver nucleoprotein, VIII, 92
- WOLF. Lactic acid, estimation of, IX, 584  
 and OSTERBERG. Estimation of sulphur in proteins, VIII, 80
- WOLFBAUER. Determination of the solidification point of fats and oils, II, 57
- WOLFF. Iodine value for linseed oil, IX, 189  
 and SCHOLZE. Blown oils, IX, 202
- WOLFF, C. Preparation of guanine, VII, 332
- WOLFF, C. H. Colorimetric tests for indigotin, v, 391
- WOLFF, J. Inulin in roasted chicory, VI, 675
- WOLFF, M. See *A. Tschirch*.
- WOLFF, P. W. Use of special burners to avoid the formation of soot by acetylene, III, 10
- WOLFFENSTEIN. See *Wackernagel*.
- WOLFFENSTEIN, R. Coffee substitutes, VI, 665
- WOLFRAM. Theobromine in cocoa nibs and husk, VI, 700
- WOLLNY. Modification of Reichert's value for fats and oils, II, 23
- WOLPIAN. Terpene in cumin oil, IV, 334
- WOOD. Composition of Lincoln wool, VIII, 683  
 Bacterial action in tan liquors, v, 100
- WOOD and MARSHALL. Formation of hydrocyanic acid in the preparation of isonitrosoantipyrine, VI, 40
- WOOD, C. H. Estimation of chloral yielded by chloral hydrate, I, 271
- WOOD, J. T. Estimation of tannins, v, 60, 61, 90
- WOODFORDE. See *Hewitt*.
- WOODHEAD. See *Green*.
- WOODMAN and BURWELL. Detection of formic acid and sodium formate as food preservatives, I, 521
- DAVIS. Estimation of benzaldehyde, IX, 286
- LYFORD. Estimation of benzaldehyde in almond extracts, III, 419
- NEWHALL. Test for caramel, v, 640
- TAYLOR. Estimation of caffetannic acid by Krug's method, VI, 658
- WOODRUFF. Preparation of aloin, VII, 141
- WOODRUFF, F. O. See *R. E. Doolittle*.
- WOODS. See *Grindley*.
- WOOTTON. See *Jones*.
- WORMLEY. Extraction of gelsemine, VII, 31  
 Size of red corpuscles, VIII, 501
- WORMLEY, T. G. Atropine and hyoscyamine, test for, VI, 308  
 Bromine as a reagent for alkaloids, VI, 189  
 Picric acid test for alkaloids, VI, 186  
 Poisoning by nicotine, VI, 242
- WORSTALL. Hydrocarbons, separation of, IX, 232  
 Paraffins, properties of, III, 3
- WORSTALL, R. A. Detection of wood turpentine oil, IV, 425
- WORSTALL, R. W. Copals, IV, 56
- WORTMANN. Yeast culture in cider manufacture, I, 218  
 of wine, I, 218
- WOTZAL, M. E. Tests for solanine, VII, 92
- WREDEN. Benzene hexahydrides, III, 42
- WRIGHT. Aconitine, composition of, VI, 258  
 Lubricating greases, determination of the water in, III, 179  
 Meat, frozen, IX, 613  
 Mydriatic alkaloid in *Lactuca muralis*, VI, 311  
 Oils, modulus of expansion of, II, 50  
 See *Cripps, Farr, Stone*.
- and BECKETT. Acetyl-derivatives of cinchona alkaloids, VI, 506
- GILL. Traube's viscosimeter, III, 157
- MITCHELL. Oils, fats and waxes, II, 4, 7  
 Saponification value for linseed oil, II, 334
- THOMPSON. Hydrolysis of soap, II, 416
- WRIGHT, A. Reaction of blood, VIII, 498
- WRIGHT, ALDER. Coconut oil, mean combining weight of the mixed fatty acids from, II, 188  
 and ALLEN, A. H. Estimation of aconitine, VI, 282
- LUFF. Alkaloids of the hellebores, VII, 79, 80  
 of sabadilla, VII, 70, 73
- WRIGHT, C. R. A. Cymene, detection of, in an essential oil, IV, 165  
 Fatty acids, combining weights of the, II, 380  
 Soap, addition of ammonium salts to, II, 419  
 and C. THOMPSON. Analysis of soap, II, 423

- WROBLEWSKI. Casein, composition of, VIII, 121  
 Glycogen-splitting enzyme and diastase in yeast, I, 212  
 Xylidines, VI, 71  
 WUERTZ. Formation of hydrocyanic acid from methylamine, VII, 463  
 WÜRTZ, G. Coffee-beans, VI, 665

## Y

- YAPLE, F. Analysis of cocoa powder, VI, 691  
 YATES. Acid value of cassia oil, IX, 355  
   *See Pickard.*  
 YEOMAN, H. *See A. G. Green.*  
 YERR. Examination of lakes, v, 538  
 YOCUM. Treatment of tannin solution with hide powder, v, 85  
 YODER, P. A. Estimation of malic acid in cane and maple products, IX, 99  
 YOSHIDA. Action of maltose on Pavy's ammoniacal cupric solution, I, 363  
 YOSHIDA, H. Composition of camphor oil, IV, 321  
 YOSHIKAWA. Estimation of lactic acid in muscle extractive, IX, 608  
 YOSHIMURA. Formation of  $\beta$ -iminazolyethylamine from fermented soja beans, VII, 350  
   and KANAI. Dried codfish, IX, 622  
 YOUNG. Specific gravity of ethyl alcohol, I, 110  
   *See Francis, Harden, Jackson, Spence.*  
 YOUNG, S. Detection of traces of gallic acid in commercial gallotannic acid, v, 22  
 YOUNG, SYDNEY. Distillation, I, 20, 21  
   and FORTEY. Distillation, I, 20  
 YOUSSEFIAN. *See Haller.*  
 YVON, P. Detection of traces of water in ethyl alcohol, I, 110

## Z

- ZALESKI. *See Nencki.*  
 ZALOCOSTAS. Constitution of spongin, VIII, 672  
 ZANDER, E. Microchemical test for chitin, VIII, 671  
 ZAY, C. E. Italian peppermint oils, IV, 371  
 ZDAREK, E. Estimation of thymol, IV, 289  
 ZEBEL, C. Extraction of cinchona bark, VI, 489  
 ZEIDLER. Separation of the constituents of crude anthracene with solvents, III, 274  
   *See Stritar.*  
 ZEISEL. Derivatives of colchicine, VII, 6  
   and FANTO. Estimation of glycerol, I, 168; II, 461, 466

- ZEISEL and STOCKERT. Colchicine, bromo-derivatives of, IX, 534  
   solutions, colloidal nature of, IX, 534  
 WITTMANN. Decomposition products of solanine, VII, 90  
 ZEISEL, S. Determination of the methoxyl numbers of essential oils, IV, 240  
 ZEISS. Immersion refractometer of, I, 25  
 ZEITSCHEL. *See Blumann.*  
   *See Hesse.*  
 ZELINSKY. Conversion of cyclohexane to benzene, IX, 237  
 ZENTHEN. Solubility of tannin extracts, v, 82  
 ZENTHEN, H. R. Estimation of non-tannins, v, 65  
 ZERR. Drying oils, IX, 184  
 ZETTL. Stability of cyanogen solutions, VII, 455  
 VON ZEYNEK. Cyanhæmoglobin, VIII, 537  
   Hæmin, preparation of, VIII, 547  
   Hæmochromogen, VIII, 550  
   Hæmoglobin, spectrum of, VIII, 521  
   Spectrophotometric quotient of methæmoglobin and oxyhæmoglobin, VIII, 690  
 ZIEMKE. Precipitin test for blood, VIII, 578  
 ZIMMERMANN. Rennet coagulation, VIII, 131  
   Sesame oil, IX, 136  
   *See Korentschewski, Möhlau.*  
 ZIMMERMANN, A. Formogelatin, VIII, 600  
 ZINNOFFSKY. Hæmoglobin, VIII, 91  
 ZINOFFSKI and DRAGENDORFF. Assay of ipecacuanha, VII, 44  
 ZIPPERER. Cocoa nibs, analysis of, VI, 689  
   husks, VI, 696  
 ZÖLLER. Estimation of caffeine, IX, 527  
 ZOLCINSKI, J. Analyses of tea, VI, 600  
 ZOLOGIECKI, R. and KLARFELD, H. Optical activity of Galician petroleum, III, 44  
 ZOTIER, V. Distinction between acetanilide and methylacetanilide, VI, 86  
 ZSIGMONDY. Gold number of proteins, VIII, 78  
   *See Benedikt.*  
   and SCHULZ. Gold number of proteins, VIII, 78  
 ZSIGMONDY, R. Colloidal character of gelatin, VIII, 589  
 ZULKOWSKY, K. Assay of ferrocyanide melt, VII, 514  
 ZUMPF. *See Ulzer.*  
 ZUNE, M. Estimation of rosin oil in turpentine oil, IV, 422  
 ZUNZ. Protein digestion products, VIII, 473, 475  
 ZYMANDI. *See Friis.*



# SUBJECT INDEX

## A

Abbé refractometer, I, 23  
 use of, in estimating sugar solutions, I, 316  
 in the examination of oils and fats, II, 42

Abel closed oil tester, III, 122  
 test for explosives, III, 595, 603, 606  
 modification of, III, 612  
 precautions in applying, III, 606  
 United States regulations for, III, 603

Abel-Pensky apparatus for the determination of  
 the flash point of kerosene, III, 126

Abietic acid, IV, 22, 23

Abrastol, III, 259, 401; VIII, 175  
 detection of, in milk, III, 260; VIII, 175  
 by the Sanglé-Ferrière test, III, 260  
 by Sinibaldi's test, III, 259  
 in wines, III, 402

Absinthe, oil of, IV, 428

Absinthiin, VII, 157

Absorption, spectra of colouring matters, V, 435

Acacia, V, 39  
 bark, reactions of, V, 47  
 oil, IV, 432

Acaroid resin oil, IV, 17  
 resins, IV, 14, 16

Acarus sacchari, presence of, in commercial cane  
 sugar, I, 354

Acenaphthene, III, 266, 268  
 behaviour of, with benzal chloride, III, 280  
 with chromic acid, III, 278  
 compound of, with picric acid, III, 275

Acetal, I, 256, 268

Acetaldehyde, I, 264  
 action of, with Fehling's solution, I, 265  
 and formaldehyde, separation of, I, 264  
 $\beta$ -naphthol test for, I, 266  
 detection of, in commercial ethyl alcohol, I  
 112  
 estimation of, I, 265  
 by Rocques' method, I, 266  
 polymerides of, I, 267  
 preparation of, I, 264  
 properties of, I, 264  
 reducing action of, I, 265

Acet-amido-ethyl salicylic acid, III, 503

Acetanilide, VI, 83  
 detection of, in antipyrine, VI, 44  
 in phenacetin, VI, 101  
 estimation of, VI, 103  
 and methtylacetanilide, distinction between,  
 VI, 86  
 and phenacetin, distinction between, VI,  
 44, 100  
 estimation of, in admixture, IX, 472

Acetanilide, Ritsert's tests for, III, 520  
 solubility of, in various solvents, III, 294

*p*-Acet-anisidine, VI, 104

Acetate of lime. See *Calcium acetate, commercial*.

Acetates, I, 490, 506  
 estimation of, I, 490  
 reactions of, I, 489  
 See also under *parent substance*.

Acetic acid, I, 488; IX, 90  
 commercial, II, 492; IX, 91  
 aluminium acetate in, IX, 91  
 formic acid in, I, 494; IX, 91  
 hydrochloric acid and chlorides in, I, 493  
 impurities in, I, 493; IX, 90  
 metals in, I, 493  
 strength of, I, 492  
 sulphuric acid and sulphates in, I, 493  
 detection of, I, 489  
 and estimation of acetic anhydride in, IX,  
 90  
 estimation of, I, 490  
 in vinegar, I, 496  
 and formic acid, action of, on mercuric  
 chloride, I, 520  
 separation of, I, 521

glacial, I, 494; IX, 92  
 boiling point of, I, 488; IX, 90  
 commercial, I, 494  
 impurities in, I, 49  
 melting point of, I, 488; IX, 90  
 effect of water on, I, 494  
 solubility of castor oil in, II, 163  
 of fats and oils in, II, 62  
 specific gravity of, I, 488, 489; IX, 90  
 from gums, I, 445  
 homologues of, I, 514  
 barium salts of, I, 518  
 detection and estimation of, in a mix-  
 ture, I, 517  
 separation of, I, 515  
 by distillation, I, 519  
 and *iso*-valeric acid, distinction between,  
 I, 525  
 aldehyde. See *Acetaldehyde*.  
 esters, detection of, I, 490  
 ether. See *Ethyl acetate*.

Acetin method for the estimation of glycerol, II,  
 460

Acetine blue, V, 327, 328

Acet-methylanilide. See *Methylacetanilide*.

$\alpha$ -Acetnaphthalide, VI, 113

$\beta$ -Acetnaphthalide, VI, 113

Aceto-acetic acid, VII, 400  
 Arnold and Liplawakep, reaction for, VII, 401

- Aceto-acetic acid, Bondi and Schwarz' reaction  
for, VII, 401  
detection of, in urine, VII, 401  
estimation of, IX, 577  
by the Polin-Hart method, IX, 577  
in blood, IX, 577  
in urine, IX, 577  
Gerhardt's reaction for, VII, 401
- Acetone, I, 104, 256  
assay of commercial, I, 109  
v. Bitto's test for, VII, 402  
detection of, I, 105; VII, 401; IX, 577  
in urine, I, 107; VII, 401  
estimation of, I, 107; IX, 576  
by Denigès' method, I, 107  
by Jolles' method, I, 107  
in blood, IX, 576  
in urine, I, 108; VII, 404; IX, 576  
in wood naphtha, I, 100  
Frommc.'s test for, IX, 577  
Legal's nitroprusside test for, I, 105; VII, 402;  
IX, 577  
Lieben's iodoform test for, I, 105; VII, 401;  
IX, 577  
Penzoldt's indigo test for, VII, 402  
Reynold's mercuric-oxide test for, VII, 402  
salicylaldehyde test for, I, 105
- Acetonyl salicylate, III, 503
- Acetophenone, III, 427  
estimation of, III, 428
- Acetphenetidines. See *Phenacetins*.
- Acetyl value for fats, oils and waxes, II, 32
- Acetyl-*p*-amido-phenyl salicylate, III, 503
- Acetylene, III, 8  
commercial, III, 8  
analyses of, III, 9  
dilution of, III, 10  
estimation of hydrogen phosphide in, III,  
9, 10  
sulphide in, III, 9  
purification of, III, 10  
detection of, in cases of poisoning, III, 10  
estimation of, III, 9  
preparation of calcium carbide for, III, 11  
pure blue, v, 602  
sky blue, v, 600
- Acetylenes, III, 7  
action of, on ammoniacal solutions of cuprous  
and silver salts, III, 7  
cuprous derivatives of, III, 7  
and other hydrocarbons, distinction between,  
III, 7  
and paraffins, separation of, III, 3  
silver derivatives of, III, 7
- Acetyl-salicylic acid, III, 503, 504; IX, 306
- Acetyl-solangustidine, IX, 541
- Acetyl-trimethylcolchic acid. See *Colchicetins*.
- Achillea oil, IV, 432
- Acid, alizarin black, SNT, v, 562  
blue BB, v, 222, 592  
GR, v, 222  
brown BB, v, 618  
dark blue SN, v, 600  
direct green G, v, 572  
green, v, 222
- Acid, alizarin grey G, v, 566  
red B, v, 554  
anthracene brown R, v, 616  
red 3 B, v, 556  
azo rubin, v, 452  
black 8 B, v, 562  
blue 6 G, v, 244, 274  
brown G, v, 163, 166, 610  
R, v, 163, 166, 610  
cerise, v, 249  
cyanine BD, v, 598  
eosin. See *Tetrabromfluorescein*.  
5 B, v, 554  
green, v, 242, 278, 453, 570  
(bluish), v, 278  
D, v, 242, 278  
extra conc., v, 278  
J. J., v, 242  
M, v, 242, 278  
SOF, v, 242  
greens, v, 462  
magenta, v, 249, 268, 452, 462, 541  
maroon, v, 249  
milling scarlet, v, 200, 548  
naphthol yellow, v, 457  
ponceau, v, 152  
rhodamine R, v, 556  
rosamine A, v, 308  
violet 4B extra, v, 258, 276  
6B, v, 258, 268, 276, 606  
7B, v, 268, 604  
BB, v, 606  
5 BK (Kalle) 6 BN, 7 BN, 5 BNS, 6 BNS,  
7 BS, 6 BW, v, 268  
4 BN, v, 258, 268, 606  
4 R, v, 308  
4 RS, v, 258, 282, 606  
violets, v, 258, 462  
yellow, v, 137, 138, 141, 144  
D, v, 138, 145  
G, v, 138, 144  
OO, v, 146  
S, v, 128
- Acids, animal, VII, 357; IX, 569  
aromatic, III, 391  
and aliphatic, comparison between, III,  
391  
classification of, III, 392  
basicity of, comparison between, III, 555  
estimation of, in potable spirits, I, 195  
fatty. See under *Fatty*.  
vegetable, I, 485  
colour reactions of, I, 486  
salts of, reactions for, I, 486
- Acme yellow, v, 139
- Acolyctine, VI, 275
- Aconine, VI, 264
- Aconite alkaloids, VI, 253; IX, 487  
assay of, VI, 279; IX, 488  
classification of, VI, 255  
toxicology of, VI, 283; IX, 489  
assay of, VI, 279; IX, 488  
physiologically, VI, 282  
detection of, toxicologically, VI, 283; IX,  
489

- Aconitine**, VI, 256, 258; IX, 487  
 constitution of, VI, 258; IX, 487  
 derivatives of, VI, 262  
 estimation of, VI, 280; IX, 488  
 hydrolysis of, VI, 263  
 pharmacology of, VI, 287  
 reactions of, VI, 261  
 salts of, VI, 260  
 toxicity of, VI, 259, 283; IX, 489  
 pseudo-Aconitine, VI, 255, 256, 270  
 salts and derivatives of, VI, 270
- Aconitum napellus**, alkaloids of, VI, 253; IX, 487  
**vulparia**, alkaloids of, IX, 488
- Acorn starch**, I, 413
- Acridine**, III, 272; VI, 162  
 colouring matters. See under *Colouring matters*.  
 hydrochloride, VI, 163  
 nitrite, VI, 164  
 orange, v, 362, 363, 366, 461, 582  
   R, v, 366  
 picrate, III, 273, 276; VI, 164  
 red, v, 461  
   B, v, 289, 302  
   2 B, v, 302  
   3 B, v, 289, 302  
   BB, v, 289  
 sulphite, VI, 164  
 yellow, v, 366, 461
- Acrolein**, I, 255  
 formation of from glycerol, II, 453
- Acrylic acid series**. See *Oleic acid series of acids*.
- Adenine**, VI, 596; VII, 321, 336  
 preparation of, from molasses residues, IX, 568
- Adipocere**, II, 397
- Agalma black B**, v, 562
- Agathin**, III, 503
- Agar-agar**, I, 437  
 commercial, diatoms in, I, 438  
 detection of, in cream, VIII, 193
- Agaric acid**, IV, 5
- Agmatine**, guanidylbutylamine, VII, 350
- Agrostemma-sapotoxin**, VII, 128
- Agurin**, VI, 595
- Air yeast**. See *Yeast, air*.
- Airol**, III, 534
- Ajowan oil**, IV, 432
- Alanine**, VII, 249  
 separation of from the hydrolysis products of proteins, VIII, 25
- d-Alanine and d-valine**, separation of, IX, 562
- Alban**, IV, 6, 158
- Albumin**, VIII, 91  
 and casein, separation of, VIII, 155  
 detection of, III, 504  
 egg. See *Egg albumin*.  
 estimation of, in milk, VIII, 155  
   in peptonized milk, VIII, 219  
 glue, VIII, 621
- Albuminoids**, VIII, 581; IX, 604  
 classification of, VIII, 582. See also *Sclero-proteins*.
- Albumins**, VIII, 33  
 and globulins, difference between, VIII, 33
- Albumins, vegetable**, VIII, 94
- Albumose**, VIII, 91
- Alcohol**. See *Ethyl alcohol*.
- Alcohols**, I, 85; IX, 1  
 acid derivatives of, I, 485  
 estimation of in essential oils, IV, 227, 264  
   in potable spirits, I, 187  
 neutral derivatives of, I, 227; IX, 18  
 resin, IV, 3  
 sesquiterpene, IX, 344
- Alcoholysis of fats**, II, 13
- Aldehyde**. See *Acetaldehyde*.  
 green, v, 570
- Aldehydes**, I, 253  
 colour reaction of, with acid rosaniline and sodium sulphite, I, 254  
 with diazobenzene-sulphonic acid in the presence of free alkali, I, 255  
 with phenol and sulphuric acid, I, 255  
 compounds of, with acid sulphites, I, 254  
 estimation of, I, 255, 256  
   in potable spirits, I, 197  
 formation of, I, 253  
 in essential oils, IV, 255  
 oxidation of, I, 254  
 properties of, I, 254  
 reduction of, I, 254
- Alder-bark**, analysis of, v, 67
- Alder-tannin**, v, 7
- Aleppo galls**, reactions of, v, 49
- Aleuritic acid**, IV, 5
- Algarobilla**, v, 37  
 reactions of, v, 50
- Algarobo**, reactions of, v, 50
- Algin**, VIII, 622  
 soluble, VIII, 623
- Alginic acid**, VIII, 622
- Algoe blue**, CF, K, 3G, v, 537  
 bordeaux, v, 537  
   3B, paste, v, 556  
 brown B, v, 538  
 dark green B, v, 574  
 green B, v, 538  
 orange R, v, 535, 556, 584  
 pink R, v, 536  
 red B, v, 536  
   5G, v, 536  
 scarlet G, v, 536, 552  
 yellow 3G, R, v, 535
- Aliphatic and aromatic acids**, comparison between, III, 391  
 hydrocarbons, III, 1
- Alizarin**, v, 206, 463, 469, 542, 604  
 and its allies, detection of, in fibre, v, 225  
 and purpurins, distinctions between, v, 215  
 black, v, 463, 558  
   P, v, 222  
   S, v, 218, 222  
   SW., v, 218  
 and aniline black, distinction between, v, 227  
 blue v, 209, 220, 463, 588, 592  
   A, AB, DNW, F, GW, R, v, 220  
 black B, v, 560  
 SW, v, 218

- Alizarin, blue, detection of, v, 447  
     logwood in the presence of, v, 408  
     S, v, 210, 220  
     detection of, v, 445  
     soluble powder, ABS, v, 220  
 bordeaux, v, 463, 544  
     B, BD, G, GG, v, 220  
 brilliant green G, v, 572  
 brown, v, 218, 463, 610  
 cardinal, v, 222  
 carmine, v, 208, 220  
 chrome black S, v, 564  
 commercial, v, 215  
     dye test for, v, 224  
 cyanine, v, 463  
     G, v, 220  
     R, v, 220, 588  
 cyanol B, v, 596  
     violet R, v, 608  
 dark green, v, 222  
     W, v, 574  
 detection of, v, 447  
     in purpurin, v, 213  
 direct blue EB, v, 596  
 for violet, v, 218  
 garnet R, v, 222  
 GG, V, v, 544  
 green, v, 302  
     B, v, 346, 352  
     G, v, 346, 352  
     S, v, 220  
     SW, v, 570  
 indigo blue, v, 588  
     S, v, 220  
 isol R, v, 608  
 maroon, v, 220, 542  
 No. 1, No. 6, No. 10, v, vi; CA, GD, GI,  
     IePRF, RG, RX, PSC, SC, SX, SX  
     extra SDF X, v, 218  
 oil. See *Turkey-red oil*.  
 orange, v, 209, 463  
     A, AO, AOP, N, OG, OR, v, 218  
     G, v, 222  
     WS, v, 580  
 paste, v, 215  
 powder W, v, 208  
 red PS, v, 554  
     S, v, 220, 469  
 sapphiroll SE, v, 598  
 S, v, 445, 542  
 violet, v, 226, 304  
 WS or S, v, 208  
 WS, W, SA, v, 220  
 yellow, v, 220  
     A, v, 218, 469, 580  
     C, v, 218  
     FS, v, 190  
     5G, v, 586  
     GG, R, v, 140, 143, 463  
     paste, v, 582  
 Alizarin-sulphonic acid, v, 208  
 Alkali blue, v, 252, 270, 462  
     3B, v, 588  
     4B, v, 590  
     6B, v, 253, 270, 455  
 Alkali, blue commercial, v, 253  
     D, v, 253, 270  
     R, v, 455  
     use of, as an indicator, II, 10  
     XG, v, 270  
 brown, v, 152  
 crimson, 161; v, 552  
 dark-brown G, 109 v, 614  
 fast red R, v, 550  
 green, v, 270, 570  
 new brown D, v, 616  
 orange G, v, 584  
 red, v, 178, 548  
     brown, 2R, v, 614  
 violet, v, 606  
     6B, v, 270  
 yellow, v, 140  
     R, v, 584  
 Alkalies, detection of, inorganic substances, I, 63  
 Alkaline earths, detection of, in organic sub-  
     stances, I, 63  
 Alkaloid in cheese, VIII, 250  
 Alkaloids, aconite. See *Aconite alkaloids*.  
     areca, VI, 208  
     calabar. See *Calabar alkaloids*.  
     cinchona. See *Cinchona alkaloids*.  
     colchicum. See *Colchicum alkaloids*.  
     conium. See *Conium alkaloids*.  
     gelsemium. See *Gelsemium alkaloids*.  
     ipécacuanha. See *Ipecacuanha alkaloids*.  
     in coca leaves, assay of, VI, 344, 345  
     lupine. See *Lupine alkaloids*.  
     mydriatic. See *Mydriatic alkaloids*.  
     of curare, VI, 474  
     of ergot. See under *Ergot*.  
     of sabadilla. See *Sabadilla alkaloids*.  
     of stavesacre. See *Stavesacre alkaloids*.  
     of the hellebores. See *Hellebores, alkaloids*.  
     opium. See *Opium alkaloids*.  
     pepper. See under *Pepper*.  
     pomegranate. See *Pomegranate alkaloids*.  
     reaction of, with acids, VI, 202  
     salts of, VI, 202  
     strychnos. See *Strychnos alkaloids*.  
     vegetable, VI, 167; VII, 1  
         behaviour of, with various indicators, III,  
         556  
         classification of, VI, 206  
         colour tests for, VI, 197  
         estimation of, VI, 178; IX, 179  
             by Keller's process, VI, 179  
             with iodine, VI, 190  
             volumetrically, VI, 181  
             with Mayers' reagent, VI, 191  
         exhaustive methylation of, VI, 204  
         formation and function of, in plants, VI,  
         168; IX, 477  
         Fröhde's reagent for, VI, 200  
         hydrolysis of, VI, 203  
         isolation of, VI, 171  
             by Kippenberger's process, VI, 178  
             by the Stas-Otto process, VI, 177  
         liquid volatile, isolation of, VI, 177  
         nomenclature of, VI, 170  
         occurrence of, VI, 167



- Alkaloids, vegetable, precipitants for**, IX, 479  
 properties of, VI, 183; IX, 479  
 reactions of, VI, 185  
   with alkalis, VI, 203  
   with auric chloride, VI, 196  
   with bromine, VI, 189  
   with Dragendorff's reagent, VI, 190  
   with iodine, VI, 189  
   with Mayer's reagent, VI, 191  
   with mercuric chloride, VI, 196  
   with methyl iodide, VI, 204  
   with oxidising agents, VI, 205  
   with picric acid, VI, 186  
   with picrolonic acid, VI, 187  
   with platinic chloride, VI, 196  
   with potassium permanganate, VI, 197  
   with Scheibler's reagent, VI, 188  
   with Sonnenschein's reagent, VI, 187  
   with tannic acid, VI, 187  
 test for the presence of, in plant materials, VI, 171  
 volatile, VI, 207, 236; IX, 480  
   estimation of, VI, 207
- Alkanet**, V, 432, 636  
 detection of, in wines, I, 181
- Alkannin**, V, 432
- Alkasal**, III, 488
- Alkyl quinolines**, VI, 155  
 tartrates, I, 539
- Allantoin**, VII, 363
- Allen-Marquardt method** for the estimation of higher alcohols in potable spirits, I, 187
- Allihn's method** for the estimation of sugars gravimetrically, I, 323
- Alloxantin**, formation of, from uric acid, VII, 363
- Alloxyproteic acid**, VII, 407
- Allspice oil**. See *Pimento oil*.
- Allyl phenols** in essential oils, IV, 290  
 colour reactions of, IV, 299  
 isothiocyanate. See *Mustard oil, volatile*.  
 sulphide, IV, 300  
 thiocarbimide, IV, 300
- Allylene dichloride**, I, 273
- Almén's tannin reagent** for milk, VIII, 155
- Almond extracts**, estimation of benzaldehyde in, III, 419  
 flavour, III, 426  
 oil, II, 69, 102; IV, 432; IX, 129  
   Bieber's test for peach-kernel and apricot-kernel oils in, II, 104; IX, 129  
   commercial, adulteration of, II, 103  
   composition of, II, 102  
   detection of apricot-kernel oil in, II, 103; IX, 129  
   of arachis oil in, II, 103  
   of lard oil in, II, 103  
   of olive oil in, II, 103  
   of peach-kernel oil in, II, 103  
   Kreis' phloroglucinol test for, II, 104  
   mixed fatty acids from, II, 102  
   nitric acid test for, II, 104  
   oleorefractometer value for, II, 44  
 water, bitter, III, 426
- Almonds, bitter, essence of**, III, 426  
 essential oil of, III, 420; IX, 349  
 assay of, III, 423  
 detection of alcohol in, III, 424  
   benzoic acid in, III, 426  
   benzyl chloride in, III, 423  
   chlorobenzaldehyde in, III, 423  
   hydrocyanic acid in, III, 424  
   nitrobenzene in, III, 424
- Alo-emodin**, VII, 148, 150
- Aloes**, VII, 137; IX, 549  
 Bornträger's test for, VII, 144, 146  
 commercial, VII, 142  
 Cripps and Dymond's test for, VII, 145, 146  
 detection of, VII, 144, 149  
   in drugs containing hydroxy-methyl-anthraquinones, VII, 149; IX, 549  
 estimation of aloin in, VII, 147  
   in mixtures, VII, 151  
 Flückiger's test for, VII, 145, 146  
 Klunge's test for, VII, 144, 146  
 preparation of aloin from, VII, 141  
 tests for, VII, 144  
 Uganda, VII, 147  
 valuation of, VII, 147
- Aloin from Barbadoes**, VII, 139  
 commercial, VII, 142  
 estimation of, in aloes, VII, 147  
 preparation of, from aloes, VII, 141  
 test for blood, VIII, 524
- Aloins**, VII, 137  
 classification of, VII, 139
- Aloresinotannol**, IV, 4
- Alphol**, III, 498
- Alpine blue**, V, 270
- Alsace green**. See *Dinitroresorcinol*
- J**, V, 130
- Alstol**, II, 488
- Alum**, detection and estimation of, in bread, I, 459  
 Logwood test for, in flour, I, 457
- Alumina cream**, preparation of, I, 309
- Aluminium acetate**, I, 510  
 oleate, II, 411  
 palmitate, II, 397  
 phenol-*p*-sulphonate, III, 395  
 salicylates, III, 488  
 thiocyanate, VII, 547
- Alypine**, detection of, IX, 495
- Amandin**, VIII, 109
- Amaranth**, V, 150; IX, 453  
 separation of, from the other coal-tar colours in meat products, VIII, 383
- Amber**, IV, 12, 18  
 oil of, IV, 21
- Ambrette oil**, IV, 432
- Amethyst**, V, 454, 461  
 detection of, V, 445  
 violet, V, 328
- Amic acids**, VII, 206
- Amides**, preparation of, VII, 204
- Amido-G-acid**, VI, 123
- Amido-naphthol red 2B**, V, 554
- o-Amido-salicylic acid**, III, 502

- Amines, VI, 1; IX, 469  
 . and ammonia, comparison between reactions of, VI, 11  
 detection of, VI, 4  
 estimation of, volumetrically by Schiff's process, VI, 9  
 physical properties of, VI, 12  
 primary, secondary and tertiary, distinctions between, VI, 4, 8  
 separation of, by acetylation, VI, 5  
   by Delépine's method, VI, 7  
   by Hinsberg's method, VI, 4  
   by Hofmann's method, VI, 5  
   from tetraalkylammonium salts, VI, 1  
   in vinasses, VI, 15  
 Amino-acetic acid. See *Glycocoll*.  
   salts of, VII, 211  
 Amino-acids, VII, 206, 212; IX, 575  
   estimation of, IX, 575  
   nitrogen by Sørensen's formaldehyde method, IX, 561  
   in urine, VII, 408  
   esterification of, IX, 561  
   formation of, in blood, IX, 575  
   by the hydrolysis of proteins, VIII, 18  
   in proteins, table of, VII, 270  
   isolation of, VII, 218  
   mono-, estimation of, VII, 262  
   formed by the hydrolysis of proteins, separation of, VIII, 21  
   ninhydrin test for, IX, 560  
   picrolonates of, IX, 562  
   putrefaction bases derived from, VII, 345  
   reactions of, VII, 217  
   separation of, VII, 218; IX, 561  
   Sørensen's estimation of, VII, 262  
   table of, VII, 213  
   Van Slyke's estimation of, VII, 263; IX, 560  
 Aminoazobenzene, V, 456  
 Amino-benzene. See *Aniline*.  
   sulphonic acids, VI, 61  
 $\alpha$ -Amino-*iso*-butylacetic acid. See *Leucine*.  
 Amino-compounds, VII, 203  
   estimation of in plant products, VII, 238  
   table of, VII, 207  
 $p$ -Amino-diphenylamine, V, 205; VI, 97  
 Aminoethane-sulphonic acid. See *Taurine*.  
 4- $\beta$ -Amino ethylglyoxaline, VII, 349  
 3- $\beta$ -Aminoethylindole, VII, 351  
 Aminoglutaric acid. See *Glutamine*.  
 $\alpha$ -Amino-glutaric acid. See *Glutamic acid*.  
 $\alpha$ -Amino- $\beta$ -hydroxypropionic acid. See *Serine*.  
 $\alpha$ -Amino- $\beta$ -iminazolyl-propionic acid. See *Histidine*.  
 $\alpha$ -Amino- $\alpha$ -naphthol, V, 206  
 $\beta$ -Amino- $\alpha$ -naphthol, V, 206  
 1-Amino-8-naphthol-2:4-disulphonic acid, VI, 127  
 1-Amino-8-naphthol-3:6-disulphonic acid, VI, 127  
 1-Amino-8-naphthol-4:6-disulphonic acid, VI, 128  
 1-Amino-2-naphthol-4-sulphonic acid, VI, 126  
 1-Amino-2-naphthol-6-sulphonic acid, VI, 126  
 1-Amino-8-naphthol-4-sulphonic acid, VI, 127  
 2-Amino-8-naphthol-3:6-disulphonic acid, VI, 128  
 2-Amino-1-naphthol-4-sulphonic acid, VI, 127  
 2-Amino-8-naphthol-6-sulphonic acid, VI, 127  
 Aminonaphthols, VI, 125  
 Aminonaphtholsulphonic acids, VI, 126  
 Amino-pentamethyl benzene, VI, 74  
 Amino- $p$ -phenacetin, VI, 104  
 $p$ -aminophenol, V, 206  
 Aminophenols, VI, 97  
 $\alpha$ -Amino-propionic acid. See *Alanine*.  
 6-Aminopurine. See *Adenine*.  
 Amino-resorcinol, V, 206  
 Amino-succinamic acid. See *Asparagine*.  
 $\alpha$ -Amino-valeric acid. See *Valine*.  
 $\alpha$ -Amino- $n$ -valeric acid, VII, 348  
 Ammonia and amines, comparison between reactions of, VI, 11  
   detection of pyridine in, VI, 137  
   estimation of, in decomposition of meat, IX, 612  
   in peptonised milk, VIII, 220  
   pyridine in, VI, 138  
   in spent gas purifying mass, VII, 523  
   method for the estimation of formaldehyde and methylamines, separation and estimation of, VI, 18  
   and trimethylamine, estimation of a mixture of, IX, 469  
 Ammoniacum, IV, 91; IX, 315  
   oil, IV, 432; IX, 432  
 Ammoniated tincture of quinine, VI, 533  
 Ammonium acetate, I, 506  
   benzoate, IX, 285  
   cyanate, VII, 538  
   cyanide, VII, 472  
   ferrocyanide, VII, 506  
   hydrogen urate, VII, 379  
   malate, I, 535  
   oleate, II, 411  
   oxalurate, VII, 362  
   picrate, III, 585  
   stearate, II, 400  
   sulphate, commercial, estimation of ammonium thiocyanate in, VII, 545  
   tartrates, I, 554  
   thiocyanate, VII, 544  
   estimation of, in spent gas purifying mass, VII, 551  
   urate, VII, 382  
   calculus, VII, 387  
 Ammoresinotannol, IV, 4  
 Amphicreatinine, VII, 317  
 Amygdalin, VII, 102  
   decomposition of, VII, 463  
 Amygdonitrile glucoside, VII, 102  
 Amyl acetate, I, 249  
   separation of, from alcohols, I, 249  
   alcohols, detection of butyl and hexyl compounds in, I, 253  
   separation of, from amyl acetate, I, 249  
   nitrite, I, 250  
   assay of, I, 253  
   commercial, I, 251  
   preparation of, I, 250  
   tests for, I, 250, 251  
*iso*-Amyl nitrite, I, 250  
*iso*-Amylamine as a putrefaction product, VII, 345  
 Amylase. See *Diastase*.

- Amylin.** See *Dextrin*.  
**Amyloid**, VIII, 91  
 $\alpha$ -**Amyrin**, IV, 3  
 $\beta$ -**Amyrin**, II, 488; IV, 3  
**Amyrol**, IV, 287, 396; IX, 343  
 $\alpha$ -**Amyrol**, II, 488  
**Analgen**, VI, 159  
**Analysis**, definition of, I, 1  
     ultimate, I, 57  
**Anamirten**, VII, 164  
**Anchovy butter**, IX, 621  
**Anchusic acid**, V, 432  
**Anchusin**, V, 432  
**Andropogon oils**, IV, 303; IX, 345  
**Anethole**, IV, 255, 291, 292  
     estimation of, in anise oil, IV, 242, 313  
     in fennel oil, IV, 242  
**Angelic acid**, IV, 328; VII, 75  
**Angelica oil**, IV, 310, 433; IX, 350  
     Japanese, IV, 311  
**Angola copal**, IV, 52  
**Angostura oil**, IV, 433  
**Anhydrodigitoxigenin**, VII, 118  
**Anhydro-ecgonine**, VI, 338  
**Anhydrolupinine**, VI, 227  
**Anhydropilosine**, IX, 538  
     physiological action of, IX, 540  
     salts of, IX, 538  
**Anilides**, VI, 82  
**Aniline**, V, 205; VI, 51  
     acetate, VI, 61  
     black, V, 312, 463, 558  
         and alizarin black, distinction between,  
         V, 227  
         constitution of, V, 313  
         in paste, V, 314  
     blue, spirit soluble, V, 284  
     blues, V, 250, 251  
         sulphonated, V, 251  
     detection of, VI, 58  
         in acetanilide, VI, 85  
     estimation of, VI, 59  
         in commercial dimethylaniline, VI, 92  
     greens, V, 259  
     homologues of, VI, 51, 63  
     hydrochloride, VI, 59  
     oils, VI, 74  
         assay of, VI, 78  
         composition of, VI, 76  
         manufacture of, VI, 74  
     orange, V, 363  
     oxalate, VI, 61  
     oxidation of, VI, 56  
     phosphate, VI, 61  
     pink, V, 323  
     red, V, 278, 472  
         detection of, in sausages, VIII, 381  
     reduction of, VI, 57  
     salts of, VI, 59  
     sulphate, VI, 61  
     sulphonic acids, VI, 61  
     tailings, VI, 81  
     tests for pure, VI, 78  
     violet, V, 324  
     yellow, V, 134, 360, 363  
**Aniline, yellow**, R, v, 156  
**Anilines**, alkylated, VI, 88  
     substituted, VI, 88  
**Anilinophenosafranine**, V, 326  
**Animal fats.** See *Tallow group of fats*.  
     and non-drying vegetable oils, distinction  
         between, II, 85  
     oleins. See *Lard-oil group of oils*.  
     tannin, V, 7, 27  
**Anime resin**, IV, 12, 57  
**Anise aldehyde**, III, 500  
     oil, IV, 244, 249, 311, 433; IX, 351  
         and star-anise oil, distinction between, IV,  
         314; IX, 351  
         estimation of anethol in, IV, 313  
         methosyl number, IV, 242  
**Anisic acid**, III, 507  
     aldehyde, estimation of, in essential oils,  
         IX, 337  
**Anisidine ponceau**, V, 148  
**Anisol red**, V, 148, 482  
**Anisole**, III, 294  
**Anisoles**, V, 299, 306  
**Annatto**, V, 408, 420, 578, 637  
     detection of, in butter, V, 663  
     in milk, VIII, 169  
**Annamese beeswax**, II, 269  
**Anthemene**, IV, 328  
**Anthemol**, IV, 328  
**Anthesterol**, II, 488  
**Anthracene**, III, 261, 267  
     acid blue, 2R, V, 602  
     behaviour of, with benzol chloride, III, 280  
         with chromic acid, III, 279  
     blue S, V, 220  
         black C, V, 568  
         SWX, V, 592  
         WG, V, 222  
         WR, V, 222  
     brown, V, 211, 610  
         R.G., V, 218  
     chromate brown EB, V, 616  
     chrome red A, V, 554  
         violet B, V, 608  
     compound of, with picric acid, III, 275  
     crude, anthraquinone test for, III, 282  
         assay of, III, 280, 282  
         constituents of, III, 265  
         behaviour of, with antimonous and bis-  
         muthous chlorides, III, 277  
         benzal chloride, III, 280  
         chromic acid, III, 278, 280  
         solvents, III, 274  
     compounds of, with picric acid, III, 274  
     detection and separation of, III, 273  
     estimation of, III, 276  
     detection of carbazole in, III, 282  
         paraffin in, III, 281  
         phenanthrene in, III, 282  
         phenylnapthylimide in, III, 282  
         estimation of paraffin in, III, 281  
     dihydride, III, 265  
     effect of solvents on, III, 262, 274  
     estimation of, in tar and pitch, III, 285  
     green, V, 302

- Anthracene, hexahydride, III, 265  
     reactions of, with metallic chlorides, III, 277  
     red, v, 186  
     violet, v, 304  
     yellow, v, 220, 580  
     BN, v, 158  
 p-Anthracene, III, 263  
 Anthracite black B, v, 172  
     D, v, 558  
 Anthracyanine 3 GL, v, 596  
 Anthraflavone G, v, 535  
 Anthragallol, v, 211, 218, 527  
 Anthranoyl-lycoctonine, IX, 488  
 Anthrapurpurin, v, 213, 218, 463  
     and alizarin, distinction between, v, 215  
     and flavopurpurin, distinction between, v, 214  
     detection of, v, 447  
 Anthraquinone, III, 263  
     blue SR, v, 598  
     effect of solvents on, III, 274  
     green GXN, v, 574  
     test for crude anthracene, III, 282  
     violet, v, 608  
 pseudo-Anthrene, III, 269, 275, 279  
 Antiarigenin, VII, 124  
 Antiarin, VII, 123  
 Antiarose, VII, 124  
 Antifebrin, VI, 85  
     and phenacetin, distinction between VI, 103  
 Antimonial wine, I, 553  
 Antimonin, VII, 447  
 Antimony, detection of, in organic substances, I, 64  
 Antinosin, III, 557  
 Antipyretics derived from quinoline, VI, 156  
 Antipyrine, VI, 37, 48  
     derivatives, VI, 45  
     detection of adulterants in, VI, 44  
     in pyramidone, VI, 49  
     estimation of, VI, 43; IX, 470  
     in migrainine, VI, 47  
     Kippenberger's method for the estimation of, VI, 43  
     nevraltine and pyramidone, distinction between, VI, 48  
     Pharmacopoeia requirements for, VI, 41  
     salicylate, III, 491  
     tests for, IX, 470  
 Antithermin, VI, 36  
 Antoxyproteic acid, VII, 407  
 Apiole, IV, 255, 291, 298  
 Apocodeine, VI, 395  
 Apollo red, v, 150  
 Apomorphine, VI, 365, 387; IX, 499  
     hydrochloride, VI, 388; IX, 499  
 Apopin oil, IV, 433  
 Aporeine, VI, 396; IX, 501  
 Aposafarine, v, 319  
 Apricot-kernel oil, II, 69, 105; IX, 129  
     Bieber's test for, II, 104  
     detection of, in almond oil, II, 103; IX, 129  
     Kreis' phloroglucinol test for, II, 104  
     nitric acid test for, II, 104  
 Arabic acid, preparation of, from gum arabic, I, 440  
 Arabin and dextrin, distinction between, I, 439  
 Arabinose, I, 400  
     reducing power of, IX, 62  
 Arachidic acid, formation of, in the estimation of arachis oil, II, 95  
     in arachis oil, II, 93  
     estimation of, II, 101  
     percentage of, II, 96  
     in rape oil, II, 123  
 Arachis oil, II, 69, 91; IX, 126  
     arachidic acid from, II, 96  
     Bellier's test for, IX, 126  
     constituents of, II, 91  
     detection of, II, 93  
     in almond oil, II, 103  
     cottonseed oil in, II, 101  
     in olive oil, II, 99, 117  
     poppy oil in, II, 101  
     rape oil in, II, 102  
     sesame oil in, II, 101  
     in sesame oil, II, 146  
     effect of temperature on the viscosity of, III, 148  
     estimation of, II, 93, 98  
     crude arachidic acid in, II, 101  
     isolation of arachidic and lignoceric acids from, II, 93  
     oleorefractometer values of, II, 44, 92  
     properties of, II, 91  
     fatty acids from, II, 93  
     Renard's process for, IX, 127  
 Arachnoidiscus Ehrenbergii in commercial agar-agar, I, 438  
 Aramdendrene, IV, 339  
 Arbacin, VIII, 91  
 Archil, v, 636, 637  
     red, v, 161  
     substitute, v, 148  
     extra, v, 150  
     G, 3 VN, v, 150  
 Arctic sperm oil. See *Sperm oil, Arctic*.  
 Areca alkaloids, VI, 208; IX, 480  
 Arecaidine, VI, 211  
 Arecaine, VI, 210  
 Arecolidine, IX, 480  
     hydrochloride, IX, 480  
 Arecoline, VI, 209  
     salts of, VI, 209  
 Argentol, VI, 160  
 Arginine, VI, 229; VII, 260; IX, 625  
     estimation of, by Van Slyke's process, VIII, 82  
     and histidine, separation of, VIII, 29  
     separation of from the products of protein hydrolysis, VIII, 29  
 Argol, I, 543  
     analysis of, by the Goldenberg 1907 method, I, 545  
     assay of, I, 545  
     detection of lead in, I, 568  
     estimation of potassium hydrogen tartrate by Oulman's method, I, 545  
 Argols, London method for, IX, 100  
 Aricine, VI, 500, 547

Aristoquinine, IX, 518  
 Armour's extract of meat, VIII, 398, 402  
 Arnica oil, IV, 434  
     yellow, V, 158  
 Arnidiol, II, 488  
 Arnold and Liplawsky's reaction for aceto-acetic acid, VII, 401  
 Aromadendral, IV, 336, 341  
 Aromatic acids. See *Acids, aromatic*.  
 Arrowroot, I, 417  
     adulteration of, I, 417  
     starch, Maranta, I, 412, 415  
         Natal, I, 412  
 Arsenic, detection of, I, 63  
     in glycerin, II, 472, 474  
     in organic substances, I, 64, 75  
     in vinegar, I, 504  
     estimation of, I, 63  
     in hops, VII, 184  
     in malt, I, 146  
 Arsenical ptomaines, VII, 355  
 Artemisia bitters, VII, 151; IX, 550  
     oil, IV, 434  
 Arum starch, I, 413  
 Asafetida, IV, 92; IX, 316  
     oil, IV, 95, 434; IX, 317  
     tincture of, IV, 95  
 Asaprol. See *Abrastol*.  
 Asaresinotannol, IV, 4  
 Asarole, IV, 255, 291, 297  
     identity of, with *d*-linalol, IX, 383  
 Asarone. See *Asarole*.  
 Asarum Canadense oil, IV, 397, 434  
     Europæum oil, IV, 397, 434  
 Asbolin, III, 349  
 Ash, alkalinity of, I, 74  
     analysis of, I, 74  
     from organic substances, estimation of, I, 72  
     ordinary constituents of, I, 73  
 Asparagine, VIII, 234  
     estimation of, VII, 241  
     in plant-products, VII, 237  
     isolation of, from vegetable juices, VII, 239  
     preparation of aspartic acid from, VII, 240  
 Asparox, IX, 614  
 Aspartic acid, VII, 240  
     estimation of, in protein hydrolysis, IX, 592  
     separation of, from the hydrolysis products of proteins, VIII, 27  
 Asphalt, III, 57; IX, 240  
     absence of oxygen in, III, 91  
     action of petroleum spirit on varieties of, III, 63  
     sulphuric acid on, III, 99, 100  
     adulteration of, III, 63  
     analysis of, III, 69, 73  
         comparison of methods for, III, 88  
         by Linton's method, III, 86, 89  
         by Sadtler's method, III, 87, 89  
         results of, III, 88  
     artificial, III, 93  
     bromine absorption for, III, 93  
     composition of, III, 60  
     detection of coal-tar pitch in, III, 65

Asphalt, determination of consistency of, III, 69  
     flowing point of, III, 76  
     loss on heating, III, 72, 76  
     melting point of, IX, 242  
     physical properties of, III, 75  
     softening point of, III, 76  
     drip point of, IX, 243  
     ductility of, IX, 242  
     estimation of bitumen soluble in naphtha, III, 80  
     in crude petroleum, III, 54  
     fixed carbon in, III, 81  
     mineral matter or ash in, III, 79, 84  
     in mineral oils, IX, 246, 249  
     organic matter, insoluble in, III, 79, 84  
     sulphur in, III, 84; IX, 247  
     total bitumen in, II, 77  
     water in, III, 73  
     examination of, III, 59  
     float test for, IX, 243  
     fluxed with paraffin oils, estimation of paraffin in, III, 82  
     fluxes, III, 95; IX, 243  
         analysis of, III, 97  
         determination of, loss of water of, III, 96  
         specific gravity of, III, 95, 101  
         physical properties of, III, 95  
     hydrocarbons in, III, 93  
     iodine absorption for, III, 92  
     lutes, tests of, III, 98  
     manufactured, III, 64  
     mastics, physical tests for, III, 97  
     natural, and coal-tar pitch, distinction between, III, 64  
         estimation of, in presence of artificial, IX, 245  
         and petroleum, separation of, IX, 245  
     occurrence of, III, 58  
     penetration of, III, 72  
     products, detection of in tars, by the dimethylsulphate test, IX, 278  
     proportion of sulphur and mineral matter in varieties of, III, 63  
     refined, III, 58  
         examination of, III, 74  
     soft, composition of, III, 61  
     substitution of coal-tar pitch for, III, 63  
     sulphur in, III, 92, 93  
     systematic examination of, with solvents of fixed purity, III, 90  
     ultimate composition of, III, 90, 92  
     for varnish-making, III, 63  
     volatility factor of, III, 88  
 Asphaltene, III, 59  
 Asphaltic oils, estimation of paraffin in, III, 82  
 Asphalt-paving mixtures, III, 65  
     penetration of, III, 98  
     Philadelphia specifications for, III, 65  
     physical tests for, III, 97  
     specifications for, III, 67  
     standard method of sizing and separating aggregate in, III, 73  
     tensile strength of, III, 98  
 Asphaltum, estimation of paraffin in, III, 82; IX, 244

- Asphaltum, natural, detection of, in coal-tar distillate, IX, 277  
 Aspirin, III, 503, 504  
     estimation of salicylic acid in, IX, 306  
 Assay, definition of, I, 1  
 Atisine, VI, 255, 277  
     alkaloids, VI, 255  
 Atlas orange, V, 139  
     red, V, 152, 548  
 Atophan, effect of ingestion of, IX, 570  
 Atractylol, IV, 287; IX, 343  
 Atractylene, IV, 253, 287  
 Atroglyceryl tropeine, VI, 302  
 Atrolactyl tropeine, VI, 302  
 Atropamine, VI, 291, 298  
 Atropic acid, VI, 292  
 Atropine, VI, 291, 294; IX, 490  
     commercial, VI, 296  
     estimation of, IX, 493  
     hydrolysis of, VI, 291  
     hyoscyamine and hyoscine, distinctions between, VI, 303  
     methobromide, VI, 296  
     reactions of, VI, 303; IX, 491  
     salts of, VI, 296  
     tests for, VI, 303; IX, 491  
     toxicological detection of, VI, 309  
     and veratrine, distinction between, VI, 307  
 Atroscine. See *l-Scopolamine*.  
 Attar of roses. See *Oil of roses*.  
 Aubepine, III, 500  
 Auramine, V, 231, 457, 461, 578  
     detection of, V, 445  
     I, II, III, V, 233  
     G, V, 233  
     O, V, 232  
 Aurantia, V, 122, 129, 462, 466, 576  
 Aureosin, V, 296  
 Auric chloride, use of as a reagent for alkaloids, VI, 196  
 Aurichlorbenzaconine, VI, 264  
 Aurin, V, 260, 270, 462, 469, 540  
     detection of, V, 445  
 Auronal black, V, 378  
 Aurotine, V, 270, 462, 582  
 Axelrod's process for the estimation of rubber in vulcanised rubber, IV, 134  
 Azalin, V, 359  
 Azarin, V, 606  
     S, V, 136, 542  
 Azindone blue GR, V, 328  
 Azine colouring matters. See under *Colouring matters*.  
     blue, V, 327  
     green, V, 461, 570  
     GB, TO, S, V, 328  
     scarlet, V, 328  
 Azines, constitution of, V, 317  
 Azo acid black, 3 BL extra, V, 564  
     yellow, V, 139  
 Azobenzene red, V, 161  
 Azo-black, V, 164, 172  
     blue, V, 196  
 Azo-blue, V, 192, 466, 588  
 Azo-brown O, V, 148  
 Azocarmine, V, 340, 462, 544  
     B, G, V, 328  
 Azococcin 7 B, V, 161, 162, 168  
     2 R, V, 148  
 Azo-colouring matters. See under *Colouring matters*.  
 Azo-compounds, secondary, V, 160  
 Azo-corinth, V, 196  
 Azo-eosin, V, 150, 542  
 Azoflavine, V, 139, 142, 146, 580  
     S, V, 146  
 Azo-fuchsin B, V, 154, 544  
     G, V, 154, 544  
     4 G extra, V, 552  
 Azo-green, V, 244, 270, 570  
 Azoimide, VI, 27  
 Azolitmin, V, 429  
 Azomauve, V, 192  
     N, V, 606  
 Azomerino black, BE, V, 566  
 Azonigrin, V, 172  
 Azo-orange R, V, 196  
 Azo-orseillin, V, 178  
 Azophenine blue R, G, V, 592  
 Azo-phloxine, V, 554  
 Azophor red, V, 203  
 Azo-reds, V, 146  
 Azo-rubin S, V, 150  
 Azo-turkey red, V, 156  
 Azo-violet, V, 184, 604  
 Azo-wool blue B, V, 600  
     violet 7 R, V, 608  
 Azoxy colouring matters. See under *Colouring matters*.  
 Azo-yellow, V, 139, 146  
 Azuline, V, 251, 270  
 Azurine, V, 251, 346, 462
- B
- Babool bark, reactions of, V, 48  
     pods, reactions of, V, 51  
 Backhousia citriodora oil, IV, 434  
 Baden acid, VI, 121  
 Badiana oil, IV, 434  
 Baeyer's acid, VI, 121  
 Bagasses oil, II, 119  
     comparison of with olive-kernel oil, II, 119  
 Balata, IV, 156, 158  
 Bale blue, V, 325  
 Ballistite, application of Abel test to, III, 599  
 Balsam, African, IV, 83  
     Canada. See *Canada balsam*.  
     Copaiba. See *Copaiba balsam*.  
     Gurjun, IV, 88, 444  
     Maracaibo, IV, 83  
     Maranham, IV, 83  
     Maturin, IV, 83  
     Oregon, IV, 79  
     Peruvian. See *Peruvian balsam*.  
     Tolu. See *Tolu balsam*.  
 Balsam-fir oil, IV, 434  
 Balsams, IV, 13, 74  
     aromatic, III, 448; IX, 294  
     analysis of, III, 454  
     cinnamic, III, 453, IX, 295

- Bamboo curare**, vi, 475  
 fibres, microscopic appearance of, in paper, i, 475
- Bananas**, i, 463
- iso-Barbaloin**, vii, 148
- Barbaloina**, vii, 139
- Barfoed's reagent**, preparation of, i, 333
- Barium caprate**, i, 525  
 caprylate, i, 525  
 citrate, i, 557  
 cyanate, vii, 538  
 cyanide, vii, 475  
 ethyl sulphate, i, 239  
 oxalate, i, 528  
 platinocyanide, vii, 534  
 succrate, i, 340.  
 thiocyanate, vii, 547  
 isovalerate, i, 525
- Bark**, estimation of tannin in, v, 94  
 mallet, ix, 396
- Barley**, i, 463  
 analysis of, ix, 5  
 estimation of starch in, i, 423; ix, 76  
 flaked, composition of, i, 464  
 flour and oatmeal, analysis of a mixture of, i, 418  
 germs, alkaloid of, vii, 36  
 leucosin of, viii, 104  
 and malt, differences between, i, 133  
 proteins in, viii, 103  
 roasted. See under *Roasted malt*.  
 starch, i, 412, 415
- Barretol**, iii, 209
- Barsilowsky's base**, vi, 66
- Barwood**, v, 431, 550, 637
- Base oils**. See *Blown oils*.
- Bases**, animal, vii, 195; ix, 560  
 classification of, vii, 195  
 imino, vii, 303  
 putrefaction. See *Plomaines*.  
 tetralkylammonium. See *Tetralkylammonium bases*.
- Basil oil**, iv, 434
- Basle blue**, v, 588  
 BB, v, 328, 461  
 R, v, 328, 461  
 RS, BBS, v, 462  
 S, v, 328
- Bassia butyracea**, ix, 147  
 latifolia, ix, 146  
 longifolia, ix, 146  
 mottleyana, ix, 149  
 tallow, ii, 71, 176; ix, 146  
 toxisperma, ix, 148
- Bassorin and dextrin**, distinction between, i, 439
- Bastard cotton oil**. See *Kapok oil*.
- Baudouin test for sesame oils**, ii, 143, 301
- Baumé's hydrometer**, i, 8  
 Table for comparison of degrees of, with specific gravity, i, 14; ix, 4  
 of different, with true specific gravity, i, 10  
 transformation of specific gravity into degrees Baumé (rational), i, 12
- Bavarian blue BSF**, v, 254  
 DBF, v, 255, 280  
 DSP, v, 272, 590  
 spirit soluble, v, 250  
 XL, v, 274
- Bay oil**, iv, 314, 435  
 California, iv, 316, 435; ix, 352
- Bdellium**, iv, 98, 100
- Bean starch**, i, 412
- Beans, cacao**. See under *Cacao*.
- Bechi's silver nitrate test for cottonseed oil**, ii, 136
- Beckerite**, iv, 18
- Beck's hydrometer**, i, 15
- Beech-nut oil**. See *Beech oil*.
- Beech oil**, ii, 131
- Beechwood creosote oil**, composition of iii, 352
- Beef, canned**, viii, 336  
 analyses of, viii, 333  
 composition of, viii, 269  
 dried, viii, 367  
 essence of, viii, 392  
 extract, analysis of viii, 420  
 creatinine and creatine in, viii, 412  
 cubes, viii, 419  
 and yeast extract, comparative composition of, viii, 419  
 fat, ii, 72, 204  
 crystallization of, ii, 318, 321  
 detection of, in lard, ii, 321  
 frozen, viii, 351, 352  
 lean, composition of, viii, 305  
 tallow, ii, 208
- Beer**, i, 149  
 composition of, i, 150  
 detection of bitter substances in, i, 161  
 dulcine in, vii, 303  
 hop-substitutes in, vii, 191  
 picric acid in, iii, 581  
 salicylic acid in, i, 163; iii, 478  
 estimation of arsenic in, i, 148  
 carbon dioxide in, i, 157  
 extract in, i, 157  
 fluorides in, i, 163  
 mineral constituents of, i, 160  
 saccharin in, i, 164  
 sulphates in, i, 161, 163  
 total nitrogen in, i, 157  
 unfermentable matter in, i, 157  
 finished the stability of, i, 164  
 optical method of determining alcohol and extract in, i, 156  
 preservatives in, i, 163  
 specific gravity of, ix, 11
- Beer-vinegar**, i, 498
- Beer-wort**, estimation of alcohol in, i, 156  
 original specific gravity of, i, 151, 155
- Beeswax**, ii, 73, 242  
 acid value of, ii, 246, 252  
 action of ether on, ii, 243  
 solvents on, ii, 243  
 adulteration of, ii, 248  
 analysis of, ii, 246, 259  
 annamese, ii, 269  
 bleaching of, ii, 244  
 effect of, on the constants, ii, 245



- Beeswax**, Buchner's number for II, 256  
 butyro-refractometer values for, II, 249  
 and cerasin, distinction between, III, 57  
 cerotic acid in, II, 243  
 Chinese, II, 268  
 detection of adulterants, II, 248  
   artificial colouring matters in, II, 262  
   carnauba wax in, II, 261, 271  
   ceresin or paraffin in, II, 257  
   colophony in II, 256  
   free stearic acid in, II, 255  
   hydrocarbons in, II, 258  
   Japan wax and other fatty substances in, II, 255  
   paraffin wax in, IX, 151  
   spermaceti in, II, 260  
   wool wax in, II, 261  
 distillation of, II, 243  
 ester value for, II, 253  
 estimation of ceresin in, II, 258  
   cerotic acid in, II, 246  
   in complex candle mixtures by Hehner's method, II, 262  
   fatty alcohols in, II, 258  
   myricin in, II, 247  
   paraffin in, II, 258  
 free acids in, II, 243  
 from combs five years old, analysis of, II, 262  
 group of waxes, II, 242  
 Indian, II, 268  
 iodine value of, II, 254  
 melissic acid in, II, 244  
 melting point of, II, 251  
 myricin in, II, 244  
 paraffin hydrocarbons in, II, 243  
 ratio of the ester and acid values of, II, 254  
 refractive power of varieties of, II, 250  
 saponification value of, II, 246, 252  
 separation of from honey, II, 242  
 solidifying point of, II, 251  
 solubility of, in chloroform, II, 249  
 specific gravity of, II, 250  
 unsaponifiable matter from, II, 261  
 Weinwurm's test for, II, 257  
 yellow, II, 242
- Beet**, estimation of sugar in, I, 360  
 sugar, I, 338  
   average composition of ash of, I, 348  
   molasses from, I, 357  
   purity of, I, 352  
   solutions clarifying of, I, 312  
   juice, analysis of, I, 360
- Belladonna**, assay of, VI, 311, 314; IX, 492  
 plaster, VI, 315
- Belladonnine**, VI, 291, 299
- Belmontine oil**, III, 118
- Bence-Jones protein**, VIII, 91
- Bengal blue**, v, 327
- Bengaline**, v, 327
- Benguela copal**, IV, 51
- Benin copal**, IX, 310
- Benne oil**. See *Sesame oil*.
- Benzacetic acid**, III, 503
- Benzaconine**, VI, 263
- Benzal chloride test for solid hydrocarbons**, III, 280  
 green, v, 241, 278
- Benzaldehyde**, III, 417; IX, 286  
 assay of, III, 423; IX, 288  
 estimation of, III, 419; IX, 286  
 green, v, 241
- Benzanalgen**, VI, 159
- Benzanilide**, vi, 87
- Benzene**, III, 199  
 action of benzal chloride on, III, 280  
   bromine on, III, 203  
   chlorine on, III, 203  
   oxidizing agents on, III, 203
- Benzene-carboxylic acid**. See *Benzoic acid*.
- Benzene, commercial**, III, 206, 222  
 distillation of, III, 207, 229  
 estimation of available benzene in, III, 207  
 grades of, III, 208  
 specific gravity of, III, 228, 229  
 tests for, III, 208  
 crude, estimation of, in denatured alcohol, I, 113
- derivatives, nomenclature of**, III, 200
- detection of**, III, 204  
   petroleum spirit in, III, 241  
   thiophenin, III, 210
- estimation of**, III, 206, 207  
   carbon disulphide in, III, 228  
   thiophen in, III, 211
- hexahydride**, III, 204
- hexahydrides, specific gravity and boiling points of**, III, 201
- production of, from coal-tar**, III, 202
- properties of**, III, 202
- ring, Kekulé's theory of the**, III, 199
- separation of, in mixtures**, III, 204  
   from petroleum spirit, III, 241  
   thiophen, III, 211
- series, members of the**, III, 199
- specific gravity of**, III, 203  
 and toluene, differences between, III, 215
- Benzenedicarboxylic acids**, III, 541
- Benzerythrene**, III, 270  
 behaviour of, with chromic acid, III, 279  
 compound of, with picric acid, III, 276
- Benzeugenol**, III, 416
- Benzidine**, VI, 108  
 colouring matters. See under *Colouring matters*.  
 estimation of, VI, 109  
 test for blood, VIII, 524
- Benzin**, III, 111, 113  
 for degreasing, III, 116  
 petroleum, purified, III, 114
- Benz- $\alpha$ -naphthalide**, VI, 113
- Benzoates**, III, 409  
 detection of, in milk, VIII, 173  
 estimation of benzoic acid in, IX, 283  
 metallic, III, 414; IX, 285  
   analysis of, III, 412  
 See also under *Parent substance*.
- Benzoazurin**, v, 590  
 G, v, 184, 588  
 3G, v, 184, 590

- Benzo-black, S, v, 558  
 blue, v, 590  
 G, v, 186  
 5G, v, 188  
 R, v, 194
- Benzo-blue black, R, v, 558
- Benzo-brown, v, 610  
 B.G., v, 166, 610
- Benzo-chrome brown, G, v, 614
- Benzo-dark green, 2G, v, 572
- Benzo-fast heliotrope, 2RL, v, 606  
 red, GL, v, 554  
 scarlet, 7BS, v, 552  
 violet R, v, 608  
 yellow, 4GL extra, v, 584
- Benzoflavine, v, 362, 368, 461, 580
- Benzoflavone, production of, v, 361
- Benzo-green, BB, v, 572
- Benzo-grey, v, 180, 560  
 S, v, 560
- Benzoic acid, III, 403, 404; IX, 279  
 and cinnamic acid, melting points of mixtures of, III, 436  
 separation of, III, 437  
 commercial, III, 406  
 detection of ammonium chloride in, III, 407  
 chlorinated compounds in, III, 407  
 cinnamic acid in, III, 407  
 essential oil in, III, 408  
 halogens in, IX, 279  
 hippuric acid in, III, 406  
 salicylic acid in, III, 406  
 sugar in, III, 407  
 derivatives of, III, 403  
 detection of, III, 409; IX, 279; 282  
 in butter, II, 311; III, 410; IX, 282  
 in cinnamic acid, III, 437  
 in coffee extract, IX, 282  
 in cream, VIII, 190  
 in essential oil of bitter almonds, III, 426  
 in foods, III, 410; IX, 280  
 in meat and fats, IX, 281  
 in milk, VIII, 173; IX, 280  
 in saccharin, III, 430  
 in wine, III, 410; IX, 280  
 effect of, in foods, III, 405  
 estimation of, III, 411; IX, 283  
 in ketchups, III, 413; IX, 284, 285  
 in meat, IX, 285  
 in milk, III, 413; IX, 284  
 in sausage, IX, 619  
 extraction of, from flesh products, III, 411; IX, 281  
 formation of, III, 404  
 in urine, IX, 574  
 from gum benzoin, III, 408  
 Jonescu test for, IX, 280  
 occurrence of, in resins, IV, 2  
 Pharmacopœia requirements for, IX, 279  
 properties of, III, 405  
 reactions of, IX, 279  
 tests for the origin of, III, 408
- aldehyde. See *Benzaldehyde*.
- anhydride, III, 417
- chloride. See *Benzoylchloride*.
- Benzoic acid, esters, III, 415
- o-Benzoic sulphinide. See *Saccharin*.
- Benzoin, analysis of, III, 451  
 Padang, III, 450  
 Palambang, III, 450  
 Penang, III, 450  
 Siam, III, 449  
 Sumatra, III, 449; IX, 294  
 tincture of, III, 452
- Benzo-indigo blue, v, 186
- Benzol. See *Benzene*, commercial.  
 commercial, separation of thiophen in, III, 235
- Benzolin, III, 111, 113
- Benzola, commercial, assay of, III, 225, 234; IX, 260  
 bulb-tube test distillation for, III, 233  
 dehydration of, III, 225  
 detection of carbon disulphide in, III, 226  
 estimation of benzene and its homologues in, III, 229  
 carbon disulphide in, III, 226  
 retort test distillations for, III, 230  
 varieties of, III, 223
- Benzo-nitrol black, v, 564  
 brown, G, v, 614  
 developer, v, 616
- Benzo-olive, v, 188
- Benzo-orange, R, v, 180, 580
- Benzo-pure blue, v, 188
- Benzo-purpurin, B, v, 194, 202, 540  
 4B, v, 177, 192, 544  
 6B, v, 192  
 10B, v, 184, 540  
 use of, in colouring sausages, VIII, 381
- Benzo-red, SG, v, 554
- Benzoresinol, IV, 3
- Benzosol, III, 345, 416
- Benzosulphinidum. See *Saccharin*.
- Benzoyl chloride, III, 417  
 oxide. See *Benzoic anhydride*.  
 tropeine, VI, 301
- Benzoyl-aminoacetic acid. See *Hippuric acid*.
- Benzoyl-cystin, VII, 245
- Benzoyl-ecgonine, VI, 336
- Benzoyl emetine, IX, 543
- Benzoyl glycine. See *Hippuric acid*.
- Benzoyl-guaiacol, III, 345, 416
- Benzoyl-methyl-guanidine, VII, 307
- Benzoyl-pseudotropine, VI, 341
- Benzoyl-sarcosine, VII, 273
- Benzyl acid black, BB, v, 568  
 alcohol and monohydric phenols, distinction between, III, 288  
 benzoate, III, 416  
 blue, S, v, 600  
 chloride, detection of, in essential oil of bitter almonds, III, 423  
 cinnamate, III, 439  
 fluorescein, v, 457  
 salicylate, III, 496  
 violet, v, 258, 272, 461, 473, 604
- Benzylamine and toluidines, physical distinctions between, VI, 64
- Benzyl- $\alpha$ -naphthylamine, VI, 116

- Berbamine, VI, 563  
 Berberine, V, 360; VI, 551; IX, 521  
     constitution of, VI, 552  
     detection of, VI, 554; IX, 521  
     in plants, VI, 555; IX, 521, 522  
     estimation of, VI, 536; IX, 521  
     reactions of, VI, 554; IX, 521  
     salts of, VI, 559  
     synthesis of, IX, 521  
 Bergamot juice, I, 559, 560  
     leaves, oil of, IV, 318  
     oil, IV, 244, 316, 435; IX, 352  
     wild, oil of, IV, 318  
 Bergaptene, IV, 316  
 Bergmann and Junk test for explosives, III, 615  
 Berlin race, V culture yeast, I, 215  
 Bertheaume's method for the separation and estimation of methylamines and ammonia, VI, 18  
 Berthelot's apparatus for the determination of boiling point, I, 17  
 Betaine, VII, 273  
     detection of, in cattle-foods, VII, 278  
     hydrochlide, preparation of, from molasses residues, IX, 563  
     salts of, VII, 274  
 Betaines, VII, 270  
 Betasterol, II, 486  
 Betel-nut alkaloids, VI, 208  
 Betle oil, IV, 435  
 Betol, III, 498  
     colour reaction of, with chloroform and alkali, III, 298  
 Betulol, IX, 343  
 Beverages containing tannin, estimation of salicylic acid in, III, 485  
     detection of saccharin in, III, 431  
     saponins in, VII, 129  
     estimation of saccharin in, III, 433  
 Bichloral-antipyrine, VI, 46  
 Biebers' test for the detection of apricot-kernel and peach-kernel oils in almond oil, II, 104  
 Biebrich acid black, ST, V, 566  
     blue (Kalle), V, 272  
     scarlet, V, 161, 162, 170, 450, 540  
 Bihhaconitine, VI, 255, 256, 271  
     salts and derivatives of, VI, 272  
 Bile, VII, 409  
     acids, VII, 410  
     detection of, IX, 578  
     Pettenkofer's reaction for, VII, 420  
     separation of, VII, 417  
     analyses of, IX, 579  
     ox, acid from, IX, 579  
     pigments, VII, 423  
     Bonanno's test for, IX, 580  
     detection of, in uride, VII, 425  
     estimation of, IX, 579  
     Gmelin's test for, VII, 425  
     Hammarsten's test for, VII, 425  
     Huppert's test for, VII, 426  
     Rosin's test for, VII, 426  
     Salkowski-Schipper's test for, IX, 580  
     tests for, VII, 425; IX, 580  
 Biliary calculi, VII, 410  
 Bilirubin, VII, 424  
 Biliverdin, VII, 425  
 Bindscheder's green, V, 310  
 Birch oil, III, 494  
 Birchwood tar oil, methoxyl number, IV, 242  
 Birotation, I, 315  
 Bisabol myrrh, IV, 98  
 Bisabolene, IV, 103; IX, 325  
 Biscuits, colouring matter in, V, 651  
 Bishop's method for the determination of the drying properties of oils, II, 38  
 Bismal, III, 534  
 Bismarck brown, V, 163, 166, 458, 461, 466, 610  
 Bismuth benzoate, III, 415  
     cerium salicylate, III, 491  
     potassium iodide as a reagent for alkaloids, VI, 190  
     salicylate, III, 489; IX, 304  
     subgallate, III, 533  
 Bitter principles occurring in medicine, detection of, VII, 138  
 Bitter-almond water, III, 426  
     estimation of cyanogen contents in, VII, 466  
 Bitumen, Callender's, IV, 152  
     estimation of residual coke in, III, 72  
     fixed carbon in, III, 81  
 Bitumens, III, 37; IX, 240  
     action of sulphuric acid on, III, 99, 100  
     classification of, III, 38  
     estimation of, in asphalt, III, 77; IX, 240  
     oxygen in, IX, 250  
     extraction of, IX, 241  
     origin of, III, 37. See also *Asphalt*.  
 Bituminous road materials. See *Road materials*, *bituminous*.  
 Biuret, VII, 290  
 Bixin, V, 420  
 Björklund's ether test for cacao butter, II, 179  
 Black acid. See under *Acid*.  
     alizarin. See under *Alizarin*.  
     aniline. See under *Aniline*.  
     anthracite. See under *Anthracite*.  
     auronal, V, 378  
     B. agalma, V, 562  
     corvan, V, 568  
     kryogen, V, 564  
     paradiamine, V, 568  
     pyrol, V, 566  
     triazol, V, 568  
 BB, benzyl acid, V, 568  
     kresol, V, 562  
 BW., carbon, V, 564  
 2 BNI, union, V, 568  
 3 B, Calcutta, V, 568  
     duatol, V, 562  
 4 B, naphthalene acid, V, 564  
     phenylene, V, 564  
     sulphocyanine, V, 564  
 4 BS, coomassie wool, V, 564  
 6 B, palatine chrome, V, 562  
 6 BG conc., thiogene, V, 564  
 base I diphenyl, V, 566  
 benzonitrol, V, 564  
 brilliant. See under *Brilliant*.

- Black clayton.** See under *Clayton*.  
 cross dye, v, 560  
 diamine. See under *Diamine*.  
 diamond. See under *Diamond*.  
 dianil, v, 108  
 diazo. See under *Diazo*.  
 direct. See under *Direct*.  
 domingo. See under *Domingo*.  
 erio-chrome. See under *Erio-chrome*.  
 F, oxychrome, v, 562  
 FC., thional, v, 566  
 FR, pluto, v, 564  
 fast. See under *Fast*.  
 G, chrome acid, v, 568  
 I, Janus, v, 562  
 immedial. See under *Immedial*.  
 induline, v, 332  
 jet. See under *Jet*.  
 katigen. See under *Katigen*.  
 liquor, I, 511  
 N, oxamine, v, 564  
 NF, oxydiamine, v, 560  
 naphthol. See under *Naphthol*.  
 naphthylamine. See under *Naphthylamine*.  
 pyrogene, v, 377  
 resorcin, v, 558  
 Sea rape oil. See *Rape oil, Black Sea*.  
 Soudan, v, 562  
 T, chromate, v, 566  
   extra, sulphur, v, 377, 566  
   phenylamine, v, 564  
 tannin, v, 558  
 thiophenol. See under *Thiophenol*.  
 thioxine, v, 378  
 victoria. See under *Victoria*.  
 vidal. See under *Vidal*.  
 violet, v, 172, 558  
 woaded, v, 558  
 wool. See under *Wool*.
- Blackley blue**, v, 252, 254, 327
- Blast-furnace tar creosote.** See *Creosote, blast-furnace tar*.
- Bleu fluorescent**, v, 343  
 de Lyon, v, 252  
 nuit, v, 284
- Blood**, aloin test for, VIII, 524  
 amino-acids in, IX, 575  
 benzidine test for, VIII, 524  
 coagulation of, VIII, 497  
 defibrinated, specific gravity of, VIII, 498  
 detection of carbon monoxide in, VIII, 533  
   on leather, VIII, 572  
   strychnine in, VI, 459  
   uric acid in, VII, 366  
 estimation of aceto-acetic acid in, IX, 577  
   acetone in, IX, 576  
   carboxyhaemoglobin in, VIII, 532  
   haemoglobin in, VIII, 560  
   lactic acid in, IX, 583  
   uric acid in, IX, 572  
 guaiacum test for, VIII, 522, 526  
 haemin test for, VIII, 574  
 laking of, VIII, 503  
 malachite green test for, VIII, 524  
 medico-legal examination of, VIII, 568
- Blood**, paraphenylenediamine hydrochloride test  
   for, VIII, 525  
   phenolphthalein test for, VIII, 525  
   precipitant test for, VIII, 577  
   reaction of, VIII, 498  
   red corpuscles from, VIII, 498  
   serum, detection of urea in, VII, 295  
   stains, examination of, VIII, 568  
   tests for, VIII, 568
- Blown oils**, II, 361  
 characteristics of, II, 363  
 Fahrion's method for the examination of, II, 367  
 fatty acids, characteristics of, II, 363, 365  
 oxidised acids, characteristics of, II, 364  
 production of, II, 38  
 solubility of, in alcohol, II, 362
- 1900 Blue** v, 345
- Blue**, acetine, v, 327, 328  
 acetylene. See under *Acetylene*.  
 acid. See under *Acid*.  
 alizarin. See under *Alizarin*.  
 alkali. See under *Alkali*.  
 alpine, v, 270  
 aniline. See under *Aniline*.  
 anthracene. See under *Anthracene*.  
 azine, v, 327
- B**, celestine, v, 346  
   formyl, v, 600  
   Heligoland, v, 592  
   oxychrome, v, 596  
   palatine chrome, v, 602  
   Peri wool, v, 598
- BS**, xylene, v, 60
- BVSI**, v, 252
- 2 B**, eboli, v, 598  
   thional, v, 604
- 6 B**, gentian, v, 251, 284
- basle**. See under *Basle*.
- bavarian**. See under *Bavarian*.
- bengal**, v, 327
- black**, v, 172  
   thion, v, 566
- Bradford**, v, 272
- brilliant**. See under *Brilliant*.
- CP, K, 3 G**, algole, v, 537
- capri**. See under *Capri*.
- china**, v, 252, 254, 284
- chlorazol**. See under *Chlorazol*.
- chrome**. See under *Chrome*.
- ciba**. See under *Ciba*.
- congo**. See under *Congo*.
- cotton**. See under *Cotton*.
- coupier's**, v, 327
- delphine**, v, 346, 352
- diamine**. See under *Diamine*.
- diaminogene**, v, 592, 600
- dianil**. See under *Dianil*.
- dianisidine**, v, 188
- diazo**. See under *Diazo*.
- diphenylamine**. See under *Diphenylamine*.
- direct**. See under *Direct*.
- eosin**. See under *Eosin*.
- erio-chrome**. See under *Erio-chrome*.
- eserine**, VII, 25

- Blue, ethyl, v, 251  
   ethylene, v, 354  
   extra R, deep, v, 345  
   fast. See under *Fast*.  
   fine, v, 251  
   fluorescent, v, 343, 346, 467  
   G, diamogene, v, 592  
     naphthalene, v, 588  
   GN, toluylene dark, v, 602  
   GR, azindone, v, 328  
   6 G, katigent chrome, v, 598  
   gallamine, v, 345, 348, 462, 592  
   glacier, v, 276  
   glycin, v, 186  
   guernsey, v, 327  
   helvetia, v, 280  
   Hessian, v, 251, 284  
   Höchst new, v, 276  
   immedial. See under *Immedial*.  
   indamine. See under *Indamine*.  
   indanthene. See under *Indanthene*.  
   indoin. See under *Indoin*.  
   indophenol, v, 588  
   intensive, v, 596  
   iris, v, 346  
   ketone. See under *Ketone*.  
   L, extra, sulphur, v, 600  
   London, v, 252  
   marine, v, 252, 254  
   melanogene, v, 380  
   Meldola's, v, 341, 348, 461  
   metamine. See *Metamine blue*.  
   metaphenylene. See *Metaphenylene blue*.  
   methyl. See under *Methyl*.  
   methyldiphenylamine, v, 280  
   methylene. See under *Methylene*.  
   milling, v, 334  
   naphthazine, v, 334  
   naphthol. See under *Naphthol*.  
   naphthyl. See under *Naphthyl*.  
   navy. See under *Navy*.  
   neutral, v, 334, 461, 590  
   new. See under *New*.  
   Nicholson's, v, 252, 270, 455  
   night. See under *Night*.  
   nile. See under *Nile*.  
   nouveau P, v, 341  
   opal, v, 251, 252, 274  
   oxamine. See under *Oxamine*.  
   P, gallanilic, v, 463  
   pacific, v, 282  
   paramine. See under *Paramine*.  
   paraphenylene. See *Paraphenylene blue*.  
   pararosaniline, v, 250  
   patent. See under *Patent*.  
   pelican, v, 327  
   phenylene, v, 341  
   Poirrier's soluble, III, 552  
   printing. See under *Printing*.  
   prussian. See *Prussian blue*.  
   pure. See under *Pure*.  
   pyrogene, v, 378  
   pyrrole, VI, 148  
   quinoline, v, 359; VI, 153  
   R, coomassie navy, v, 594  
  
 Blue, R, janus, v, 594  
   (Kalte) neutral, v, 280  
   naphthylene, v, 341, 590  
   2 R, naphthogene, v, 598  
   resorcin, v, 344, 346, 462, 588  
   rosaniline, v, 251, 447, 455, 463  
   S, benzyl, v, 600  
   SR, anthraquinone, v, 598  
   silk, v, 254  
   soluble. See under *Soluble*.  
   spirit, v, 251, 284, 588  
   thiogene. See under *Thiogene*.  
   thionine. See under *Thionine*.  
   thioxine. See under *Thioxine*.  
   titan ingrain, v, 592  
   toluidine. See under *Toluidine*.  
   tolylene. See under *Tolylene*.  
   triazol. See under *Triazol*.  
   Turnbull's, VII, 506, 526  
   ultramarine, v, 588  
   urania, v, 356  
   vat indigo, v, 588  
   victoria. See under *Victoria*.  
   water, v, 252, 254, 284, 455  
   Williamson's, VII, 506  
   wool. See under *Wool*.  
  
 Boiling point, determination of, I, 17  
 Bois de rose, oil of, IX, 366  
 Boldo oil, IV, 435  
 Bonanno's test for bile pigments, IX, 580  
 Bondi and Schwarz's reaction for aceto-acetic acid, VII, 401  
 Bone fat, II, 72, 204  
   valuation of, II, 205  
   grease. See *Bone fat*.  
   tallow. See *Bone fat*.  
 Bonnet's test for formaldehyde, I, 258  
 Borates, detection of, in cream, VIII, 190  
   in milk, VIII, 174  
   estimation of, in cream, VIII, 194  
   in milk, VIII, 174. See also under *Parent substance*.  
 Borax, action of glycerol on, II, 454  
 Bordeaux B, v, 152, 452, 466  
   BX, v, 168, 170  
   COV, v, 178  
   extra, v, 178, 542  
   G, v, 170, 542  
 Boric acid, estimation of, in butter, II, 312  
   in meat extracts, VIII, 425  
   in pickle for meat curing, VIII, 371  
 Borneo camphor, IV, 277  
   tallow, II, 71, 176; IX, 149  
   detection of, as a substitute for cacao butter, II, 179  
 Borneol, IV, 254, 277; IX, 342  
   and isoborneol, distinctions between, IV, 379; IX, 342  
   esters of, IV, 278  
   specific rotation of, IV, 254; IX, 342  
 iso-Borneol, IV, 278  
 Bornträger's test for aloes, VII, 144, 146  
 iso-Bornyl chloride, IV, 181  
 Bornylene, IV, 183  
   constitution of, IV, 185

- Boron compounds, detection of, in butter, II, 311, 312
- Boronia oil, IV, 435
- Boro-salicylic acid, III, 503
- Borosaly, III, 503
- Boswellic acid, IV, 5
- Bottlenose oil. See *Sperm oil, Arctic*.
- Botulism, VIII, 321
- Bouillon cubes, analyses of, IX, 616
- Bovine, IX, 614
- Bovox, IX, 614
- Bovril, VIII, 398, 421; IX, 614
- Bradford blue, V, 272
- Brand's extract of meat, VIII, 398
- Brandt's reagent, preparation of, VII, 92
- Brandy, I, 200  
     colouring matters in, V, 655
- Brani castrol, II, 488
- Brazil nut oil, II, 70, 132  
     wood, V, 431, 550, 635, 637
- Brazilein, V, 431
- Brazilin, V, 431
- Bread, I, 458  
     adulteration of, I, 459  
     detection of alum in, I, 459  
         plaster of Paris in, I, 460  
     estimation of alum in, I, 459  
     gluten, VIII, 102  
     wheaten, analysis of, I, 459
- Breakfast foods, composition of, I, 464
- Brilliant acid blue FF, V, 596  
     alizarine blue, V, 316  
         G, V, 356  
         GR, R, V, 356  
         3 R, V, 604  
         G and R (Bayer), V, 358  
         cyanine 3 G, V, 592, 594  
     anthrasurol G, V, 604  
     azurine B, V, 592  
         5 G, V, 184, 590  
     benzo green B, V, 572  
     black, V, 558  
         B, V, 172  
     congo, V, 542  
         G, V, 178  
         R, V, 194, 544  
     cotton blue, V, 280  
     cresyl blue, 2 B, V, 596  
     croceine, V, 168, 544  
         M, V, 161, 162  
     double scarlet 3 R, V, 542  
     fast blue 2 G, V, 598  
     glacier blue, V, 282  
     green, V, 461, 570  
         detection of, V, 445, 453  
     hessian purple, V, 198  
     induline (Kalle), V, 329  
     orange, V, 139  
     orseille C, V, 550  
     ponceau, V, 150  
         4 R, V, 152  
     purpurin, V, 192  
         R, V, 544  
     red, V, 550  
     scarlet, V, 542
- Brilliant scarlet, R, V, 542  
     yellow, V, 122, 128, 146, 198, 462, 578  
     S, V, 138
- Brissemoret-Derrien's reaction for digitoxin and digitalin, VII, 121
- British gum. See *Dextrin, commercial*.
- p-Brom-acetanilide, VI, 86
- Bromides, detection of, IX, 587, 589
- Bromindigo FB, V, 537
- Bromine, as a reagent for alkaloids, VI, 189  
     commercial, detection of bromoform in, I, 282  
     detection of, in organic substances, I, 62  
         in presence of ferro- and ferri-cyanides, IX, 587  
     estimation of, in organic substances, I, 63  
     value for oils and fats, II, 26
- $\alpha$ -bromocamphor, IV, 207
- $\beta$ -Bromocamphor, IV, 209
- $\pi$ -Bromocamphor, IV, 209
- $\alpha$ -bromocamphor- $\pi$ -sulphonic acid, IV, 210
- $\alpha\pi$ -bromochlorocamphor, IV, 210
- Bromoform, I, 281  
     detection of, in commercial bromine, I, 282
- $\alpha\alpha$ -Bromonitrocarnphor, IV, 207
- Bromostychnine, VI, 443
- Brönner's acid, VI, 121
- Broom, alkaloid of, VII, 68; IX, 541
- Brown A, B sulphamine, V, 156  
     acid. See under *Acid*.  
     alizarin, V, 218, 463, 610  
     alkali. See under *Alkali*.  
     anthracene. See under *Anthracene*.  
     B, algole, V, 538  
         V, cibandone, V, 538  
     domingo alizarin, V, 620  
     immedial, V, 616  
     indanthrene, V, 538, 616, 620  
     metachrome, V, 618
- Bismarck, V, 163, 166, 458, 461, 466, 610
- catechu, V, 166, 610
- chrome. See under *Chrome*.
- cinnamon, V, 163
- clayton. See under *Clayton*.
- cloth. See under *Cloth*.
- congo. See under *Congo*.
- cotton, V, 612
- cryogene, V, 380
- diamine. See under *Diamine*.
- dianol. See under *Dianol*.
- direct. See under *Direct*.
- durophenine. See under *Durophenine*.
- eclipse. See under *Eclipse*.
- fast. See under *Fast*.
- G, benzonitrol, V, 614  
     diphenyl fast, V, 174  
     Helindone, V, 538  
     Monochrome, V, 614  
     OO, triazol, V, 618  
     Pegu, V, 618  
     pyrol, V, 618  
     sulphur, V, 616  
     thioxine, V, 614
- GC, thiogene, V, 618
- GG, katigen yellow, V, 616
- 3 G, dianil, V, 616

- Brown 3 G, oxamine, v, 616  
     Hessian. See under *Hessian*.  
     indoxyl, v, 385  
     kryogene. See under *Kryogene*.  
     Manchester. See *Manchester brown*.  
     Mikado. See under *Mikado*.  
     NP, NPJ, v, 150  
     naphthine, v, 156  
     naphthylamine, v, 148, 610  
     O, crumpsall direct fast, v, 612  
     oxydiamine, v, 616  
     paramine, v, 616  
     phenyl, v, 610  
     phenylene, v, 163, 166, 458  
     pluto, v, 616  
     pyramidol, v, 196  
     pyrogene. See under *Pyrogene*.  
     R, janus, v, 614  
     R, 2 B, naphthamine, v, 616  
     4 R, pyrogene, v, 618  
     resorcin, v, 163, 166  
     soudan, v, 136, 463  
     tetrazo, v, 163  
     thiophene, v, 614  
     V, oxychrome, v, 616  
     W, palatine chrome, v, 616  
 Brucine, vi, 464  
     detection of, in strychnine, ix, 510  
     estimation of in nux vomica, vi, 469  
     reactions of, vi, 465  
     toxicology of, vi, 465, 466  
 Brusmer-liver oil, ii, 221  
 Buchner's numbers for waxes, ii, 256  
 Buchu oil vi, 435; ix, 353  
 Buckthorn, v, 637  
 Buckwheat starch, i, 413  
 Buddeised milk. See under *Milk*.  
 Buffalo rubine, v, 550  
 Burchardt-Liebermann test for cholesterol, ii, 483  
 Butter, ii, 302  
     addition of to margarine, ii, 314  
     analysis of ii, 15, 306  
     ash in, ii, 305  
     azo-dyes in ii, 308, 309  
     and butter substitutes, distinction between, i, 524  
     cacao. See *Cacao butter*.  
     colouring matters in, ii, 308; v, 663  
     cow's, ethyl ester value for, ii, 190  
     detection of benzoic acid in, ii, 311; iii, 410; ix, 162  
     of boron compounds in, ii, 311, 312  
     of cinnamic acid in, ix, 163  
     of fluorides in, ii, 312; viii, 690  
     of mustard oil in, ii, 316  
     of  $\beta$ -Naphthol in, ii, 311, 312  
     of palm oil in, by Halphen's method, ii, 310  
         by the Liebermann-Storch method, ii, 310, 316  
     of salicylic acid in, ii, 311, 312  
     difference, figure for, ix, 625  
     digitonin test for, ix, 164  
     estimation of ash in, ii, 305, 308  
         of boric acid in, ii, 312  
         of curd in, ii, 305, 307; ix, 162  
     Butter, estimation of fat in, ii, 307; ix, 158  
         of lactose in, ii, 308  
         of salicylic acid in, ii, 313; ix, 162  
         of salt in, ii, 308; ix, 162  
         of water in, ii, 304, 306; ix, 155  
     examination of, ii, 302  
     fat, ii, 72, 204, 279; ix, 152  
         adulteration, detection of, ii, 280, 298  
         Baudouin's test for, ii, 301  
         butyro-refractometer values, ii, 281  
         composition of, ii, 279; ix, 152  
         detection of coconut-oil in, ii, 284, 296, 301; ix, 153  
         of palm-kernel oil in, ii, 301  
         of sesame oil in, ii, 301  
         of vegetable fats in, ii, 301; ix, 163  
         determination of specific gravity of, ii, 296  
         examination of, ii, 369  
         fatty acids from, ii, 279, 280; ix, 152  
         Foam test for, ii, 299; ix, 154  
         Halphen's test for, ii, 300; ix, 154  
         Hehner and Angell's test for, ii, 287  
         Hink's test for, ii, 301  
         Köttstorfer value for, ii, 286, 297  
         Lallnent's test for, ii, 288, 297; ix, 77, 153  
         melting point of, ii, 279  
         microscopical appearance of, ii, 298  
         preparation of, from butter, ii, 290  
         rancidity of, ii, 313, ix, 165  
         refractive power of, ii, 42  
         Reichert-Meissl values for, ii, 283, 294; ix, 152  
         saponification of, ii, 279, 286, 296  
         stearic acid in, ii, 280  
         table of constants for, ii, 290  
             showing the relation between soluble and insoluble acids from, ii, 288  
         tests for, ii, 298; ix, 154  
         Valenta test for, ii, 299  
         Wanklyn's test for, ii, 299  
         Wollny's refractometer for, ii, 291  
         Zeiss' refractometer for, ii, 391  
     goa, ii, 71, 182  
     milk. See under *Milk*.  
     nutmeg, ii, 71, 182  
     Phulwara, ii, 71, 187  
     phytosteryl acetate test for, ii, 301; ix, 163  
     Polenske value for, ii, 295  
     preparation of butter fat from, ii, 290  
     preservatives in, ii, 310  
     rancidity of, ii, 313; ix, 165  
     regulations for, in various countries, ii, 303, 304  
     yellow. See *Dimethyl-amino-azobenzene*.  
 Button lac, iv, 67  
 Butyl chloral. See *Butyric chloral*.  
 Butylamine as a putrefaction product, vii, 352  
 iso-Butylamine as a putrefaction product, vii, 345  
 Butylhypnal, vi, 46  
 Butyrates, i, 523  
 iso-Butyrates, i, 523  
 Butyric acid, i, 522  
     and caproic acid, distinction between, i, 525  
     separation of, from acetic and valeric acids, i, 515, 523



Butyric and valeric acids, distinction between,  
I, 523  
iso-Butyric acid, I, 523  
Butyric chloral, I, 273  
hydrate, I, 273  
Butyro-refractometer, II, 42, 281  
Byerlyte, III, 94  
Bynedestin, VIII, 104  
Bynin, VIII, 104

## C

Cacao beans, VI, 685  
component parts of, VI, 696  
protein matter in, VI, 698  
roasted, VI, 686  
cacao butter in, II, 177  
sugar in, VI, 703  
theobromine in, VI, 700  
butter, II, 71, 176; VI, 701  
adulteration of, II, 178; VI, 717  
Björklund's ether test for, II, 179; VI, 717  
composition of, II, 177  
constants for, VI, 718  
detection of beeswax and paraffin wax in,  
II, 178  
of Borneo tallow as a substitute for, II,  
179  
of coconut oil in, II, 180, 189  
of dika fat as a substitute for, II, 179  
of vegetable oils in, II, 178  
of tallow in, II, 178, 180  
estimation of, VI, 715  
of coconut fat in, VI, 719  
ethyl-ester value for, II, 190  
group, II, 66, 71, 176  
mixed fatty acids from, II, 71, 178  
percentage of, in the roasted beans, II, 177  
properties of, II, 177  
substitutes for, II, 179; VI, 720; IX, 150  
and its substitutes, distinction between, IX,  
150  
starch, VI, 698  
Cachou de Laval, V, 374, 612  
Cadaverine, VII, 348  
Cadinene, IV, 186, 253, 287; IX, 315, 325  
Cadmium potassium iodide as a reagent for alka-  
loids, VI, 190  
Cafamarine, VI, 657  
Caffearine, VI, 647  
Caffeidine, VI, 585  
Caffeidine-carboxylic acid, VI, 584  
Caffeine, VI, 579, 581; VII, 321  
in cacao beans, VI, 700  
citrate, VI, 589  
in coffee, VI, 646  
derivatives of, VI, 595  
detection of, IX, 525  
effect of heat on, VI, 582  
estimation of, VI, 590; IX, 526  
in cocoa, VI, 709  
in coffee, VI, 608, 609, 611, 656  
in tea, VI, 606  
by Dvorkowitsch's process, VI, 608  
by Gomberg's process, VI, 612  
by Stahle Schmidt's process, VI, 606

Caffeine, extraction of, VI, 590, 606  
in guarana, VI, 683  
isomer of, IX, 525  
physiological action of, VI, 582; IX, 528  
reactions of, VI, 584  
salts of, VI, 588  
sodium salicylate, assay of, IX, 526  
solubility of, III, 294; VI, 583  
synthesis of, from xanthine, VI, 580  
toxicity of, VI, 582; IX, 528  
Caffeol, VI, 650  
Caffetannic acid, V, 7, 24; VI, 468, 645  
estimation of, in coffee, VI, 657  
Caffyn's liquor carnis, VIII, 398  
Cajuput oil, IV, 249, 318, 436  
Calabar, alkaloids of, VII, 24; IX, 536  
assay of, VII, 27  
Calabassen-curare, VI, 476  
Calamenenol, IX, 353  
Calamus oil, IV, 436; IX, 353  
Calcium acetate, I, 507  
commercial, assay of, I, 507  
detection of formates in, I, 507  
benzoate, III, 414  
butyrates, I, 523  
carbide, III, 11  
carbonate, detection of, in urinary deposits,  
VII, 384  
casein, VIII, 118, 123  
citrate, I, 556; II, 566  
assay of, I, 563, 566  
commercial. See *Citrate of lime*.  
and tartrate, distinction between, I, 554  
cyanamide, VII, 557; IX, 589  
cyanate, VII, 538  
cyanide, VII, 475  
ethyl sulphate, I, 239  
lactate, VII, 446  
meconates, VI, 414  
 $\beta$ -naphthol sulphonate. See *Abrastol*.  
oxalate, I, 527, 528  
detection of, in urinary deposits, VII, 384  
in urine, IX, 574  
formation of, in urinary calculi, VII, 388  
and tartrate, distinction between, I, 554  
paracasein, VIII, 126  
phosphate, in urinary deposits, VII, 384, 388  
racemate, I, 554  
and tartrate, distinction between, I, 554  
saccharate, detection of, in cream, VIII, 193  
in milk, VIII, 167  
sarcolactate, VII, 450  
sucrate, I, 340  
tartrate, I, 554  
assay of, I, 547  
citrate, racemate and oxalate, distinction  
between, I, 554  
Calcium-ammonium meconate, VI, 421  
Calculi, fusible, VII, 388  
urinary, VII, 385; IX, 580  
Calcutta black, 3 B, V, 568  
Calico-printing, use of gum arabic in, I, 443  
tragacanth in, I, 444  
Californian petroleum, III, 41  
Calisaya bark, VI, 479

- Callender's bitumen, IV, 152  
 Callitrolic acid, IV, 5  
 Calumba, VI, 575  
 Calvert's carbolic acid powder, III, 309  
 Cameline oil, II, 70, 132  
 Campanulin, V, 342, 350, 461, 604; VII, 271, 284  
 Campeachywood, V, 635  
 Camphene, IV, 168, 182  
     constitution of, IV, 185  
     formation of, from *iso*-borneol, IV, 279  
     production of, from pinene hydrochloride, IV, 181  
 Camphor, IV, 191  
     artificial, preparation of, IV, 191  
     Borneo, IV, 277  
     bromo-derivatives of, IV, 207  
     carboxylic acid, IV, 206  
     compound tincture of, VI, 429  
     constitution of, IV, 202  
     crude, examination of, IV, 197  
     derivatives of, IV, 202, 205  
      $\alpha$ -derivatives, IV, 202, 207  
      $\beta$ -derivatives, IV, 202, 208  
      $\pi$ -derivatives, IV, 203, 209  
     detection of, in linaloe oil, IX, 367  
     estimation of, IV, 198  
         in camphor oil, IV, 323  
         in camphorated oil, IV, 201  
         in celluloid and xylonite, IV, 199  
         in liniment, IV, 199  
         by the optical activity, IV, 198  
         in spirits of camphor, IV, 200  
     homologues of, IV, 210  
     liniment, IV, 196  
         estimation of camphor in, IV, 198  
     oil, IV, 320, 436; IX, 353  
         composition of, IV, 321; IX, 353  
         estimation of camphor in, IV, 323  
         heavy, IV, 323  
         light, IV, 323  
     optical activity of, IV, 198  
     origin of, IV, 191  
     oxidation of, IV, 203  
     oxymethylene, IV, 206  
     phenyl-hydrazone, IV, 205  
     physical properties of, IV, 193  
     physiological properties of, IV, 195  
     production of, from camphene, IV, 183  
     racemic, IV, 193  
     semicarbazone, IV, 205  
     separation of, from alcohol, IV, 200  
     specific rotation of, IV, 194  
     spirit of, IV, 196, 200  
      $\beta$ -sulphonic acid, IV, 208  
      $\pi$ -sulphonic acid, IV, 209  
     synthesis of, IV, 202  
     synthetic, artificial and natural, differences between, IV, 201  
      $\beta$ -thiol, IV, 209  
     water, IV, 196  
 Camphorated oil, IV, 196  
     analysis of, IV, 201  
 $\alpha$ -Camphorene, IX, 354  
 Camphoric acid, IV, 203  
 Camphoronic acid, IV, 203  
 Camphorquinone, IV, 206  
 Camphors in essential oils, IV, 257  
     and resins, separation of, IV, 8  
 Camwood, V, 431, 610  
 Canada Balsam, IV, 79, 80, 82; IX, 312  
     oil of, IX, 312  
     flakes, composition of, I, 464  
 Canadian petroleum, III, 41  
 Canadine, VI, 574  
     salts of, VI, 574  
 Canaigre, V, 38  
     reactions of, V, 48  
 Cananga oil, IV, 436; IX, 382  
 Canarin, detection of, V, 447  
 Candlenut oil, II, 70, 148; IX, 138  
     commercial, II, 149  
     properties of, II, 149  
     uses of, II, 148  
 Candles, complex, analysis of, by *Hehner's* method, II, 262  
     containing spermaceti, analyses of, II, 267  
     free from spermaceti, analyses of, II, 266  
     use of *carnaúba* wax in making, II, 272  
 Cane sugar, I, 338; IX, 43  
     action of alkalis on, I, 298  
     analysis of, in brewing, IX, 9  
     commercial, *Acarus sacchari* in, I, 354  
     adulterations of, I, 353  
     ash from, I, 345, 347, 348  
     assay and valuation of, I, 351  
     detection of starch-sugar as an adulterant, I, 354  
     dextrose in, I, 351  
     estimation of invert sugar in, I, 351  
         of organic matters, not sugars, I, 350  
         of sucrose in, I, 351  
         of water in, I, 343  
     fungus spores in, I, 354  
     refining value of, I, 352  
     compounds of, with metallic oxides. See *Sucrates*.  
     with sodium salts, I, 341  
     detection of, I, 302, 341  
     in milk, VIII, 166, 202  
     determination of specific rotation in the presence of glucose, I, 312  
     effect of heat on, I, 338  
     estimation of, I, 306, 342  
     in adulterated maple products I, 389  
         in cocoa, VI, 713  
         in condensed milk, I, 370  
         by fermentation, I, 298, 342  
         in infant's foods, VIII, 234  
         by inversion, IX, 43  
         invert sugar in presence of, IX, 39, 42  
         in molasses, I, 357; IX, 45  
         in plant extracts, IX, 65  
         in presence of lactose, IX, 62  
             of raffinose, I, 313, 569  
         small amounts of invert sugar in, I, 328  
         in wines, I, 171  
     extraction of, I, 341  
     factors for calculating the amount of copper to the corresponding quantity of, I, 328  
     in honey, detection and estimation of, I, 367

- Cane sugar**, hydrolysis of, I, 297  
 inversion of, by citric acid, IX, 48  
 incomplete, IX, 51  
 molasses from, I, 357  
 polarimetric estimation of, in the absence of other substances, I, 306  
 refractive index of solutions of, I, 316  
 rotation of, I, 338  
 solubility in alcohol of, I, 339  
 solution density of, IX, 21  
 solutions, table of the elevation of the boiling point of, I, 339  
 tables showing relative specific gravity of, with other sugars, I, 294  
 specific gravity of, I, 338
- Canella oil**, IV, 437
- Canna starch**, I, 412, 413
- Canned foods**, estimation of tin in, IX, 612  
 meat. See under *Meat*.
- Cannibene**, IV, 186
- Caoutchouc**, detection of, in mineral lubricating oils, III, 171
- Capaivic acid**, IV, 5
- Caparrapi oil**, IV, 437
- Caper tea**, VI, 638
- Capri blue**, V, 341, 342, 461  
 GN, V, 346  
 NO, V, 592
- Caprinic acid**, IV, 329
- Caproic acid**, distinction between isovaleric and butyric acids, I, 525
- Caps**, examination of, III, 586
- Caramel**, V, 639  
 analysis of, in brewing, IX, 7  
 detection of, V, 639, 656  
 in vanilla essence, III, 521  
 in vinegar, IX, 96  
 in wines, I, 179
- Carana elemi**, IV, 96
- Caraway oil**, IV, 244, 249, 324, 437
- Carbamic acid**, VII, 286
- Carbamide**. See *Urea*.
- Carbazol**, III, 271  
 compound of, with picric acid, III, 276  
 detection of, in crude anthracene, III, 282  
 effect of solvents on, III, 274  
 yellow, V, 180, 580
- Carbinol**. See *Methyl alcohol*.  
 bases, V, 235
- Carbohydrate analysis**, use of enzymes in, IX, 625
- Carbohydrates**, estimation of, in plant extracts, IX, 64  
 Fenton's test for, I, 302  
 hydrolysis of, I, 297  
 of the starch group, I, 405, 406  
 uniformity of specific gravity of solutions of, I, 289, 290
- Carbolic acid**. See *Phenol*.  
 disinfecting powders, III, 308, 332  
 estimation of phenol in, III, 309  
 of sulphurous acid in, III, 311  
 of tar oil in, III, 310  
 oil, estimation of naphthalene in, III, 247
- Carbon black BW**, V, 564
- Carbon black BW**, dioxide, absorption of, by Wetzol potash bulbs, I, 57  
 estimation of, in beer, I, 157  
 disulphide, detection and estimation of, in commercial naphthas and benzols, III, 226  
 estimation of, in benzene, III, 228  
 estimation of, I, 57  
 monoxide, detection of, in blood, VIII, 533  
 hæmoglobin. See *Carboxyhæmoglobin*.  
 poisoning, VIII, 536  
 papers, testing of, V, 689
- Carbonyl-ferrocyanides**, VII, 532
- Carbostyryl**, VI, 156
- Carboxyhæmochromogen**, VIII, 551
- Carboxyhæmoglobin**, VIII, 529  
 estimation of, in blood, VIII, 532  
 spectrum of, VIII, 530
- Cardamoms oil**, IV, 437; IX, 354
- Cardinal red S**, V, 249
- Caricari elemi**, IV, 96
- Carius' method** for the estimation of halogens, I, 63
- Carlsberg bottom yeasts**, I, 214
- Carminamide**, V, 422
- Carminaphtha**, V, 448, 463
- Carmine lake**, V, 423  
 red, V, 422
- Carminic acid**, V, 422
- Carmoisin**, V, 150, 540
- Carnahuba wax**. See *Carnauba wax*.
- Carnauba wax**, II, 73, 270  
 composition of, II, 270  
 constants for, II, 271  
 detection of, in beeswax, II, 261, 271  
 in soap, II, 272  
 estimation of, in mixtures, II, 272  
 influence of, on the melting point of mixtures containing it, II, 272  
 unsaponifiable matter from, II, 261  
 use of, for making candles, II, 272
- Carnine**, VII, 337; VIII, 289
- Carophyllene**, IV, 186
- Carotol**, II, 485
- Carpaine**, VII, 1
- Carpamic acid**, VII, 2
- Carrageenin**, VIII, 622
- Carrot oil**, IV, 437
- Carthagea bark**, VI, 480
- Carthamin**, V, 433
- Cartier's hydrometer**, I, 15
- Carvacrol**, IV, 213, 254, 287
- Carvestrene**, IV, 179; IX, 324
- Carvone**, IV, 212  
 estimation of, IV, 214  
 in caraway oil, IV, 324  
 and limonene, separation of, IV, 216
- iso-Carvone**, IV, 216
- Carvotanacetone**, IV, 212
- Caryophyllene**, IX, 325
- Casan pink**, V, 306  
 (Gerber), V, 288
- Cascarilla oil**, IV, 437
- Casein**, VIII, 140  
 action of acids on, VIII, 121  
 of bases on, VIII, 123

- Casein, action of formalin on, VIII, 125  
 of heat on, VIII, 124  
 of rennet-enzyme on, VIII, 125  
 of salts on, VIII, 124  
 and albumin, separation of, VIII, 155  
 ash-free, preparation of, VIII, 116; IX, 595  
 change of, to paracasein, VIII, 126  
 commercial relations of, VIII, 115  
 composition of, VIII, 119  
 detection of, in cream, VIII, 193  
 determination of the refractive index of, VIII, 136  
 estimation of, VIII, 131, 138; IX, 596  
 in milk, VIII, 155  
 in paper, I, 478  
 in peptonised milk, VIII, 219  
 glue, VIII, 620  
 hydrolysis products of, VIII, 120  
 molecular weight and valency of, IX, 596  
 physical properties of, VIII, 118  
 preparation of, VIII, 116
- Caseinates, VIII, 123; IX, 595
- Caseinogen, VIII, 91  
 amino acids formed by the hydrolysis of, VIII, 20  
 preparation of, VIII, 74
- Caseoses, estimation of, in peptonised milk, VIII, 219
- Casimirol, II, 488
- Cassella's immedial yellow D, v, 376
- Cassia oil, IV, 437, 443, 445; IX, 354  
 adulterations in, III, 445; IX, 293  
 detection of a mixture of colophony and petroleum in, III, 445  
 estimation of cinnamic aldehyde in, III, 441
- Castor bean, proteins of, VIII, 110
- oil, II, 71, 159  
 acetyl value of, II, 164  
 adulteration of, II, 161  
 behaviour of, with mineral oils, II, 163  
 with petroleum spirit, II, 163  
 butyro-refractometer values for, II, 161  
 commercial, II, 161  
 composition of, II, 160  
 constants of the mixed fatty acids from, II, 161  
 detection of adulteration of, by the solubility in alcohol, II, 162  
 coconut oil in, II, 164  
 cottonseed oil in, II, 164  
 foreign fixed oils in, II, 164  
 in copaiba balsam, IV, 89  
 oleic acid in, II, 162  
 poppyseed oil in, II, 164  
 rosin oil in, II, 161  
 seal oil in, II, 164  
 sesame oil in, II, 164  
 effect of blowing on, II, 164, 367  
 estimation of, in mixtures, II, 165  
 group, II, 66, 71, 159  
 Hehner value of, II, 164  
 mixed fatty acids from, II, 71, 161  
 oleo-refractometer value, II, 44  
 physical properties of, II, 159  
 preparation of turkey-red oil from, II, 167
- Castor oil, production of floridin by the distillation of, II, 164  
 ricinoleic acid from, II, 160  
 rotation of, II, 159, 164  
 saponification value of, II, 169  
 solubility of, in alcohol, II, 162  
 in glacial acetic acid, II, 163  
 specific gravity of, II, 161  
 viscosity of, II, 162  
 effect of temperature on, III, 148
- Catalase, VIII, 12, 15  
 in yeast, I, 213
- Catechin, v, 28, 412
- Catechol, III, 335, 336, 340  
 ethers of, III, 342  
 and homocatechol, distinction between, III, 342  
 methyl ether. See *Guaiacol*.  
 and pyrogallol, distinction between, III, 341  
 reactions of, v, 51  
 tannins, v, 8
- Catechol-phthalein, III, 546
- Catechu, v, 33, 412, 637; IX, 395  
 brown, v, 166, 610  
 decomposition products of, v, 55  
 detection of, in tea, VI, 620  
 and gambier, distinction between, v, 34  
 reactions of, v, 43
- Catechu-tannic acid, v, 27
- Catechu-tannin, v, 7
- Catigene black brown N, v, 380
- Catsups, estimation of benzoic acid in, III, 413; IX, 284, 285
- Cattle feed, colouring matters in, v, 651  
 foods, detection of ricin in, VIII, 110
- Cattu italiano, v, 380
- Caucasian petroleum. See *Petroleum, Caucasian*.
- Caulosterol, II, 487, 488
- Caviare, IX, 622  
 composition of, VIII, 460
- Cayenne linaloe oil, IX, 366  
 pepper, VII, 57  
 detection of, in vinegar, I, 504
- Cayota, v, 37
- Cazeline oil, III, 118
- Cazeneuve's mercuric oxide test for foreign colouring matter in wines, I, 178
- Cedar-leaf oil, IV, 327, 437
- Cedar-nut oil, II, 70, 149
- Cedar-wood oil, IV, 244, 325, 438
- Cedrat oil, IV, 438
- Cedrela oil, IV, 326  
 wood oil, IV, 438
- Cedrene, IV, 186, 253, 287; IX, 325
- Cedrenes. See *Sesquiterpenes*.
- Cedrol, IV, 287, 326; IX, 343
- Celery oil, IV, 327, 438; IX, 356
- Celestine blue, B, v, 346
- Celluloid, estimation of camphor in, IV, 199  
 use of camphor in the manufacture of, IV, 197
- Cellulose, I, 429; IX, 77  
 acetate filaments, VIII, 668  
 action of alkaline solutions on, I, 432  
 hypochlorites on, I, 431  
 nitric acid on, I, 431

- Cellulose**, Schweitzer's reagent on, I, 431  
 estimation of, IX, 77  
 in crude fibre, I, 437  
 free carbonyl groups in, I, 432  
 in infants' foods, VIII, 234  
 in wood and vegetable fibres, I, 435  
 hydrates, I, 430  
 mercerised, I, 432  
 nitrates, III, 560  
 plant, classification of, I, 433  
 purification of, in the laboratory, I, 435  
 separation of, from dextrin, I, 428, 435  
 from starch, I, 435  
 from sugar, I, 435  
 solvents of, I, 430  
 triacetate, I, 432  
 yeast, I, 209
- Cement**, tests of, III, 98
- Centigrade and Fahrenheit degrees**, table for comparison of, III, 619
- Cephaeline**, VII, 39; IX, 542, 543  
 salts of, VII, 40; IX, 543
- Cerastine**, V, 150
- Cereal starches**, I, 417
- Cereals**, analysis of, I, 450, 451; VIII, 108  
 colouring matters in, V, 651  
 estimation of starch in, I, 424; IX, 76  
 proteins in, I, 452; VIII, 96
- Ceresin**, III, 57  
 and beeswax, distinction between, III, 57  
 detection of, in beeswax, II, 257  
 estimation of, in beeswax, II, 258  
 colophony in, IV, 29  
 and paraffin, separation of, IX, 257
- Cerise, acid**, V, 249
- Cerotic acid** in beeswax, II, 243, 246
- Cetrarin**, VIII, 621
- Cetyl alcohol** from spermaceti, II, 274  
 palmitate in spermaceti, II, 274
- Cevadic acid**. See *Tiglic acid*.
- Cevadilline**, VII, 71
- Cevadine**, VII, 70, 73  
 hydrolysis of, VII, 74  
 salts of, VII, 74
- Cevine**, VII, 76  
 oxide VII, 76
- Chairamine**, VI, 500, 546
- Chamomile oil**, German, IV, 329, 438  
 Roman, IV, 328  
 oils, IV, 249, 328, 438
- Champaca oil**, IV, 438; IX, 357
- Charcot's crystals**, VII, 202
- Chavibetol**, IV, 255, 291
- Chavicol**, IV, 255, 291
- Cheese**, VIII, 240  
 alkaloids in, VIII, 250  
 analysis of, VIII, 250, 254; IX, 600  
 Camembert, VIII, 252  
 Cheddar, VIII, 241, 250  
 coatings, VIII, 249  
 colouring matters in, V, 663  
 cream, manufacture of, VIII, 242  
 detection of copper in, VIII, 258  
 Dutch, VIII, 251  
 Emmentaler, VIII, 251
- Cheese**, estimation of fat by the Polenske method, IX, 600  
 Ratzliff-Schmid-Bondzynski method, IX, 600  
 nitrogenous compounds in, VIII, 256  
 fat in, VIII, 246, 252, 254, 255; IX, 600  
 Gorgonzola, VIII, 251  
 iron in, VIII, 258  
 lactic acid in, VIII, 247, 256  
 manufacture of, VIII, 241  
 microscopical examination of, VIII, 259  
 mineral salts in, VIII, 247  
 preservatives in, VIII, 249  
 ripening of, VIII, 243, 249
- Chcken-leaf oil**, IV, 439
- Chenocholic acid**, VII, 416
- Chenopodium oil**, IV, 427, 439
- Cheno-taurocholic acid**, VII, 414
- Cherry water**, III, 427
- Cherry-laurel oil**, III, 420  
 water, III, 427  
 estimation of cyanogen contents in, VII, 466
- Chervil oil**, IV, 439
- Chestnut**, V, 38  
 extract, analysis of, V, 67  
 oak, American, reaction of, V, 44  
 bark, IX, 396  
 reactions of, V, 47  
 tannin, V, 7
- Chestnut-wood**, analysis of, V, 57  
 extract, analysis of, V, 66  
 reactions of, V, 42
- Chicago orange**, V, 158
- Chicken**, composition and analysis of, VIII, 430
- Chicle**, IV, 161
- Chicory**, analysis of, VI, 672, 674  
 ash of, VI, 653  
 aqueous extract of, VI, 659  
 commercial, VI, 674  
 composition of, VI, 674  
 detection of, in coffee, VI, 671  
 estimation of fat in, VI, 656  
 extracts, VI, 678  
 detection of, in coffee extracts, IX, 532
- China blue**, V, 252, 254, 284
- Chinamine**. See *Quinamins*.
- Chinese beeswax**, II, 268  
 insect wax, II, 73, 272  
 vegetable tallow, II, 71, 181  
 wood oil. See *Tung oil*.
- Chinoline**. See *Quinoline*.
- Chinovin**. See *Quinovin*
- Chironol**, II, 488; IV, 3
- Chironolic acid**, IV, 5
- Chitin**, VIII, 670
- Chitinoids**, VIII, 670
- Chloral**, I, 268  
 action of absolute alcohol on, I, 269  
 of water on, I, 269  
 alcoholate and chloral hydrate, distinctions between, I, 270  
 detection of, I, 271  
 estimation of, I, 271  
 hydrate, I, 269  
 boiling point of, I, 270

- Chloral hydrate and chloral alcoholate, distinctions between, I, 270  
 detection of, I, 271  
 estimation of, I, 271  
 solidifying point of melted, I, 270
- Chloral-antipyrine, VI, 45
- Chloralformamide, I, 274
- Chloramine yellow, V, 372
- Chloranil, III, 340
- Chloranil-violet, V, 256
- Chloranisidine P, V, 554
- Chloranisine violet R, V, 608  
 yellow GG, V, 586
- Chlorantine red 4 B, V, 552
- Chlorazol blue, V, 596  
 brilliant blue, 12 B, V, 602  
 fast yellow B, V, 586
- Chloric ether, I, 280
- Chlorin. See *Dinitroresorcinol*.
- Chlorinated ethyl chloride. See *Ethylidene chloride*.
- Chlorine, detection of free, in commercial chloroform, I, 276  
 detection of, in organic substances, I, 62  
 estimation of, in organic substances, I, 63
- Chlorobenzaldehyde, detection of, in essential oil of bitter almonds, III, 423
- $\alpha$ -Chloro- $\beta$ -bromocamphor, IV, 209
- $\alpha$ -Chlorocamphor, IV, 208
- $\beta$ -Chlorocamphor, IV, 209
- $\pi$ -Chlorocamphor, IV, 209
- Chloroform, I, 274; IX, 18  
 boiling point of, I, 278  
 commercial, I, 276  
 detection of alcohol in, I, 278, 279  
 ether with, I, 278  
 ethyl chloride in, I, 277  
 ethylene dichloride in, I, 277  
 free chlorine in, I, 276  
 hydrochloric acid in, I, 276  
 hypochlorous acid in, I, 276  
 estimation of alcohol in, I, 278, 279  
 specific gravity of, I, 280  
 detection of, I, 274  
 in essential oils, IV, 247  
 in sandal-wood oil, IV, 393  
 in the presence of large quantities of alcohol, I, 274  
 estimation of, I, 275  
 and ethylidene chloride, distinction between, I, 248  
 methylated, I, 277  
 and methylene dichloride, distinction between, I, 281  
 physical properties of, I, 274  
 pure, I, 277  
 purification of, from water and alcohol, I, 279  
 specific gravity of, I, 280  
 spirit of, I, 280  
 test for purity of, I, 277  
 use of, for preserving urine, I, 280
- Chlorogenic acid, VI, 646  
 detection of, IX, 531
- Chlorophenine G, V, 372  
 orange R, V, 582
- Chlorophenyl salicylate, III, 498
- Chlorophyll, V, 636
- Chlorsalol, III, 498
- Chocolate, VI, 693  
 analysis of, VI, 705  
 definition of, VI, 704  
 estimation of oxalic acid in, IX, 97  
 of sugar in, VI, 714  
 manufacture of, VI, 687  
 milk, VI, 695, 705  
 nut, VI, 695, 705
- Cholalic acid, VII, 414  
 choleic and deoxycholeic acids, separation of, VII, 418
- Choleic acid, VII, 416  
 cholalic and deoxycholeic acids, separation of, VII, 418
- Cholestenone, II, 482
- Cholesterol, II, 479; IX, 223  
 Buchardt-Liebermann test for, II, 483; IX, 226  
 and iso-cholesterol, separation of, II, 484  
 detection of, II, 482  
 dibromide, II, 480  
 esters, estimation of, IX, 224  
 estimation of, II, 489  
 by method of Adrien Grigaut, IX, 226  
 by method of Windaus, IX, 224  
 in animal tissues, IX, 223  
 formation of, in calculi, VII, 387  
 hydrochloric acid test for, II, 483  
 isolation of, II, 489  
 Moleschott's test for, II, 483  
 occurrence of, II, 479  
 oxidation of, II, 482  
 and phytosterol, separation of, II, 491  
 plant, II, 486  
 properties of, II, 479  
 Salkowski's test for, II, 483  
 Schiff's test for, II, 483  
 of yeast, II, 488
- iso-Cholesterol, II, 484
- Cholesterols, vegetable, II, 484  
 classification of, II, 485, 486
- Cholesteryl acetate, II, 480  
 benzoate, II, 480  
 chloride, II, 481  
 esters, II, 480  
 oleate, II, 481  
 palmitate, II, 481  
 propionate, II, 480
- Cholestrophane, VI, 587
- Cholic acid. See *Cholalic acid*.
- Choline, VII, 276  
 conversion of, into neurine, VII, 275  
 detection of, in cattle foods, VII, 278  
 in ipecacuanha root, VII, 41  
 and neurine, distinctions between, VII, 275  
 as a putrefaction product, VII, 352
- Choline-aldehyde. See *Muscarine*.
- Choloidic acid, VII, 417
- Chondrigen, VIII, 624
- Chondrin, VIII, 625
- Chondroitic acid, VIII, 626
- Chondroitin, VIII, 626
- Chondroitin-sulphuric acid, VIII, 626; IX, 574

- Chondroproteins**, VIII, 91  
**Chondrosin**, VIII, 626  
**Chromate black T**, v, 566  
**Chrome acid black G**, v, 568  
   blue, v, 255, 272, 590  
   brown RO, v, 148  
   fast-blue FR, v, 604  
   fast-brown A, v, 620  
   green, v, 256, 272, 570  
     G, v, 574  
   leather, analysis of, ix, 414  
   patent black DG, v, 566  
     green, v, 176  
     violet, v, 256, 462, 606  
       (Bayer), v, 272  
       (Geigy), v, 262, 272  
     yellow, v, 580  
       D, v, 158  
**Chromine G**, v, 373  
**Chromotrope**, v, 156  
   2 B, 10 B, 8 B, v, 184  
   2 R, v, 184, 548  
**Chrono Glabra oil**, iv, 439  
**Chrysamin**, v, 463, 466, 578  
   detection of, v, 447  
   G, v, 177, 178  
   R, v, 190, 580  
**Chrysaniline**, v, 360, 363, 368  
**Chrysanthemum oil**, iv, 329  
**Chrysarobin**, v, 227  
**Chrysotropic acid** from belladonna root, vi, 311  
**Chrysaurein**, v, 139  
**Chrysene**, III, 267, 270  
   behaviour of, with benzal chloride, III, 280  
   with chromic acid, III, 279  
   compound of, with picric acid, III, 276  
   effect of solvents on, III, 274  
   reactions of, with metallic chlorides, III, 277  
**Chryseolin**, v, 139  
**Chrysocreatinine**, VII, 317  
**Chrysogene**, III, 270  
   behaviour of, with chromic acid, III, 279  
**Chrysoidine**, v, 134, 156, 458, 461  
   R, v, 156  
   yellow, v, 576  
**Chrysoln**, v, 135, 137, 139, 142  
**Chrysolin**, v, 292, 302, 457, 462  
**Chrysophanic acid**, v, 227, 228  
   and chrysarobin, distinctions between, v, 228  
**Chrysophenin**, v, 198, 202, 578  
**Ciba blue 2 B**, v, 537  
   bordeaux B, v, 536, 556  
   green G, v, 538  
   grey G, B, v, 538  
   heliotrope, v, 537, 608  
   red G, v, 536  
   scarlet G, v, 536, 552  
   violet B, v, 537, 608  
     R, v, 537  
**Cibanone brown B**, V, v, 538  
   orange R, v, 535  
   yellow R, v, 535  
**Cibil's fluid extract**, ix, 614  
**Cider**, I, 187  
   separation of tannin from, ix, 393  
**Cider-vinegar**, I, 497; ix, 94  
   adulteration of, with distilled vinegar, ix, 95  
   ash of, I, 497  
   distinction between pure and imitation, I, 497  
**Cigar smoke**, vi, 252  
**Cinchofulvic acid**, vi, 483  
**Cinchomeric acid**, vi, 147  
**iso-Cinchomeric acid**, vi, 147  
**Cinchona alkaloids**, vi, 479, 484; ix, 514  
   amorphous, vi, 543  
   detection of, in commercial quinine sulphate, vi, 526  
   quinicine and cinchonine, distinction between, vi, 545  
   anhydro-, vi, 545  
   classification of, vi, 498  
   constitution of, vi, 501; ix, 515  
   detection of, in quinine sulphate, vi, 518  
   estimation of, vi, 487  
     by titration, vi, 496; ix, 514  
   function of, ix, 478  
   properties of, vi, 503  
   separation of, vi, 490, 496  
   test for, ix, 515  
   bark, red, vi, 479, 486  
   barks, alkaloids in, vi, 484  
     assay of, vi, 486  
     composition of, vi, 481  
     extraction of, vi, 489  
     identification of, vi, 481  
     varieties of, vi, 479  
   ledgeriana seeds, alkaloids in, ix, 514  
**Cinchonamine**, vi, 499, 547  
**Cinchona-red**, vi, 483  
**Cinchonicine**, vi, 499, 544  
   and amorphous alkaloids, distinction between, vi, 545  
**Cinchonidine**, vi, 499, 537  
   cinchonine and quinidine, separation of, vi, 495  
   detection of, in quinine sulphate, vi, 519, 522  
   and quinine, distinction between, vi, 514  
   salts of, vi, 538  
   sulphate, vi, 539  
**Cinchonine**, vi, 499, 540  
   cinchonidine and quinidine, separation of, vi, 495  
   constitution of, vi, 501  
   detection of, in quinine sulphate, vi, 522, 525  
   hydrochloride, vi, 542  
     sodium chloride in, ix, 520  
   and quinine, distinction between, vi, 514  
   sulphate, vi, 542  
**Cinchotannic acid**, v, 7, 482  
**Cinchotannin**, vi, 482  
**Cinchotine**, vi, 499, 542  
**Cineol**, iv, 254, 284; ix, 343  
   estimation of, iv, 285  
   in eucalyptus oils, iv, 339; ix, 359  
**Cineolic acid**, iv, 285  
**Cinnamein**, estimation of, in Peruvian balsam, ix, 295  
**Cinnamene**, III, 440



- Cinnamic acid**, III, 436  
 and atropic acid, distinction between, VI, 292  
 and benzoic acid, melting points of mixtures of, III, 436  
 separation of, III, 437  
 as a germicide, III, 437  
 detection of, III, 437; IX, 291  
 in commercial benzoic acid, III, 407  
 in the presence of benzoic acid, III, 437  
 in urine, IX, 291  
 estimation of, III, 438; IX, 292  
 in presence of benzoic acid, IX, 292  
 occurrence of, in resins, IV, 3  
 reactions of, III, 437; IX, 291  
 aldehyde, III, 440; IX, 292  
 detection of, in oil of cinnamon, III, 444  
 estimation of, III, 441  
 in essential oils, IX, 336  
 balsams, III, 453; IX, 295  
 esters, III, 438
- Cinnamon bark oil**, IX, 356  
 brown, V, 163  
 cinnamic aldehyde in, III, 441  
 essential oil of, I, 255  
 leaf oil, III, 446; IX, 356  
 oil, adulterations of, III, 444; IX, 293  
 detection of cinnamic aldehyde in, III, 444  
 of eugenol in, III, 444  
 of oil of cloves in, III, 445  
 oils, IV, 439, 443; IX, 292, 354
- Cinnamyl alcohol**, III, 439  
 cinnamate, III, 439  
 cocaine, VI, 339  
 tropeine, VI, 301
- Citral**, IV, 267  
 and citronellal, separation of, IV, 273  
 estimation of, IX, 337  
 in essential oils, IV, 270  
 in lemon-grass oil, IV, 308  
 formula of, IX, 344  
 in lemon oil, IV, 352
- Citrate of iron and quinine**, VI, 531  
 of lime, analysis of, IX, 109
- Citrates**, I, 555, 565  
 detection of, I, 555  
 estimation of, I, 555  
 in milk, VIII, 160  
 See also under *Parent substance*.
- Citric acid**, I, 555  
 action of, with resorcinol, I, 487  
 British Pharmacopœia requirements for, IX, 114  
 commercial, detection of lead in, I, 557  
 of sulphuric acid in, I, 557  
 impurities in, I, 557; IX, 114  
 tartaric acid in, I, 558  
 detection of, I, 555  
 tartaric acid in, IX, 114  
 estimation of, I, 555; IX, 112  
 in citric acid juices, I, 562  
 in the presence of heavy metals, I, 557  
 of other acids, IX, 112  
 juices, I, 559  
 assay of, I, 561
- Citric acid, liquors, assay of**, I, 558; IX, 110  
 and malic acid, separation of, I, 534  
 and oxalic acid, separation of, I, 556  
 and tartaric acid, separation of, I, 556
- Citron oil**, IV, 439
- Citronella oil**, IV, 244, 303, 304, 439; IX, 343  
 adulteration of, IV, 306  
 composition of, IV, 305  
 estimation of geraniol in, IV, 366; IX, 328  
 standards for, IV, 307
- Citronellal**, IV, 264, 269  
 and citral, separation of, IV, 273  
 constitution of, IV, 269  
 detection of, IV, 269  
 estimation of, IV, 269, 270, 273  
 isomeric forms of, IX, 344
- Citronellic aldehyde**. See *Citronellal*.
- Citronellol**, IV, 254, 263; IX, 341  
 formula of, IV, 263; IX, 341  
 and geraniol, separation of, IV, 259, 264  
 in otto of rose, IX, 329
- Citronellyl acetate**, IV, 263
- Citronin**, V, 128, 459, 578
- Citronine B or 2 B**, V, 146
- Citrullol**, VII, 158
- Citrullus colocynthis**, substances present in the water extract from, VII, 158
- Claret, palatine chrome**, V, 554  
 red B, V, 540
- Clayton cloth red**, V, 544  
 scarlet, V, 548  
 fast black D, V, 562  
 blacks, V, 314  
 grey S, V, 562  
 greys, V, 314  
 wool brown, V, 172  
 yellow, V, 143, 374, 580
- Clemantine Giroflé**, V, 338
- Clerget's method for the estimation of specific rotation**, I, 312
- Cleve's  $\beta$ -acid**, VI, 120  
 J-acid, VI, 120
- Clionasterol**, II, 486
- Cloth brown**, V, 612  
 G, R, V, 180  
 oils, II, 511  
 examination of, II, 513  
 liability of, to inflame spontaneously, II, 512  
 orange, V, 180, 580  
 red B, V, 544  
 (Bayer), V, 168  
 (Oehler), V, 168  
 3 B extra, V, 172  
 G, V, 168; V, 544  
 (Oehler), V, 168  
 3 G, V, 168; V, 544  
 yellow GH, V, 584
- Clove, essential oil of**, I, 255  
 oil, IV, 244, 249, 250, 330, 440; IX, 358  
 detection of, in bay oil, IV, 315  
 of oil of cinnamon in, III, 445  
 estimation of eugenol in, IV, 294  
 methoxyl number, IV, 242  
 preparation of eugenol from, IV, 293

- Clovene, IV, 186; IX, 325  
 Clupanodonic acid, II, 225  
 Clupeine, VIII, 91  
 Coagulin, VIII, 621  
 Coaguloses, VIII, 495  
 Coal, dry distillation of, III, 13  
   gas, detection of cyanogen in, VII, 456  
   estimation of cyanogen in, VII, 456  
   of naphthalene in, III, 245; IX, 266  
   manufacture, analysis of spent purifying mass in, VII, 514  
   estimation of ammonium thiocyanate in the spent purifying mass from, VII, 551  
   of cyanogen in spent purifying mass, VII, 514  
   of sulphur in spent purifying mass, VII, 22  
   oil, III, 117  
 Coal-fish liver oil, II, 221  
   effect of blowing on, II, 367  
 Coal-tar, III, 20  
   acids, estimation of, in creosote oils, III, 375, 379, 384  
   and wood-tar creosote, distinction between, III, 359  
   creosote oil. See *Creosote oil, coal-tar*.  
   cresylic acid from, III, 315  
   cyclic hydrocarbons from, III, 197  
   distillation, composition of the principal fractions from, III, 198  
   detection of natural asphaltum in residues of, IX, 277  
   of petroleum pitch in residues from, IX, 277  
   dyes, behaviour of wool with, VIII, 687  
   detection and separation of, in sausages, VIII, 381  
   effect of solvents on, IX, 452  
   examination, V, 470  
   identification of, V, 645  
   solubility of, V, 444  
   estimation of anthracene in, III, 285  
   naphtha. See *Naphtha, coal-tar*.  
   pitch, III, 29  
   breaking point determination, III, 31  
   detection of, in asphalt, III, 65  
   estimation of anthracene in, III, 285  
   of volatile organic matter in, III, 30  
   evaporation test for, III, 32  
   formation of, in dry distillation, III, 14  
   free carbon determination, III, 32  
   melting-point determination, III, 30, 32  
   and natural asphalt, distinction between, III, 64  
   slide test for, III, 32  
   softening-point determination, III, 31, 32  
   substitution of, for asphalt, III, 63  
   tests, III, 30  
   twisting-point determination, III, 30  
   and water-gas pitch, differences between, III, 33  
 Cobalt potassium cyanate, VII, 539  
 Cobaltcyanides, VII, 532  
 Coca, amorphous bases of, VI, 341  
   estimation of the alkaloid in fluid extract of, VI, 344  
   leaves, VI, 344  
   assay of, VI, 345  
   estimation of cocaine in, VI, 350  
 Cocaic acid, VI, 341  
 Cocaine, VI, 321  
   amorphous, VI, 342  
   bases allied to, VI, 338  
   benzoate, VI, 327  
   commercial, examination of, VI, 328  
   decomposition products of, VI, 336  
   detection and separation of, IX, 494  
   estimation of, VI, 349  
   in coca leaves, VI, 350  
   hydrochloride, VI, 326  
   commercial, VI, 329  
   manufacture of, from coca leaves, VI, 348  
   MacLagan's test for, VI, 332, 335  
   reactions of, VI, 323  
   salts and esters of, VI, 326  
   Schaefer's test for the purity of, VI, 334  
   substitutes, detection of, IX, 495  
   tests for, VI, 322  
   in the presence of eucaines, VI, 334  
   toxicological identification of, VI, 326  
 d-Cocaine, VI, 338  
 Cocamine, VI, 340  
 Cocatannic acid, VI, 344  
 Coccerin, V, 422  
 Coccin, V, 148, 452  
 Coccinin, V, 148  
   B, V, 148  
 Cocculin, VII, 164  
 Cocculus berries, poisoning by, VII, 163  
   indicus, bitters of, VII, 160  
 Cocethyline, VI, 339  
 Cochineal, V, 148, 421, 550, 635, 636, 637  
   ammoniacal, V, 550  
   carmine, V, 423  
   detection of, in sausages, VIII, 380  
   detection of, in wines, I, 181  
   examination of, V, 422  
   red A, 3 R, V, 544  
   scarlet G, V, 150, 548  
   R, V, 548  
   2 R, V, 148, 548  
   4 R, V, 150  
 Cochlearia oil, IV, 440  
 Cocin, new, V, 150  
 Cocoa, VI, 685  
   alkaloids in, VI, 700  
   analysis of, VI, 687, 705  
   butter, VI, 701  
   colouring matters in, V, 659  
   essence, VI, 690  
   estimation of cocoa-red in, VI, 710  
   of fibre in, VI, 707  
   of oxalic acid in, IX, 97  
   of pentosans in, VI, 697  
   of starch in, VI, 711; IX, 73  
   of sugar in, VI, 713  
   of theobromine and caffeine by Kunze's method, VI, 709

- Cocoa extract, VI, 690  
   fat, VI, 701  
     estimation of, VI, 715  
   germ from, VI, 700  
   husks, VI, 696  
     analysis of, VI, 688  
   nibs, VI, 698  
     analysis of, VI, 687  
     ash from, VI, 703  
     composition of, VI, 698  
   powder, VI, 690  
     adulteration of, VI, 721  
     estimation of saccharin in, III, 436  
 Cocoa-red, VI, 699  
   estimation of, in cocoa, VI, 710  
 Coconut fat, estimation of, in cacao butter, VI, 718  
   oil, II, 72, 187  
     adulteration of, II, 189  
     composition of, II, 13, 188  
     detection of, in butter, II, 180, 189, 301  
       fat, II, 284, 296  
       in cacao butter and lard, II, 180, 189  
       in other oils and fats, II, 189  
       in tallow, II, 213  
     ethyl ester, value of, II, 189  
     group, II, 66, 72, 187  
     mixed fatty acids from, II, 72, 188  
     specific gravity of, II, 187  
     uses of, II, 188  
   oleine, II, 190, 191  
   stearine, II, 190  
 Codamine, VI, 354, 363, 367, 396  
 Codeine, VI, 354, 363, 365, 390; IX, 500  
   and colchicine, distinction between, VII, 5  
   constitution of, VI, 356  
   detection of, VI, 392  
   estimation of, VI, 393, 433  
   hydrochloride, VI, 391  
   • phosphates, VI, 391  
   sulphate, VI, 392; IX, 500  
 pseudo-codeine, VI, 395  
 Cod-liver oil, II, 73, 213  
   adulteration of, II, 216  
   butyro-refractometer values for, II, 218  
   colour tests for, II, 219  
   composition of, II, 214  
   detection of iodine in, II, 215  
     of other oils in, II, 217, 219  
     of vegetable oils in, II, 219  
   effect of blowing on, II, 367  
     of oxidation on, II, 218  
   examination of, II, 215  
   free fatty acid in, II, 219  
   gadolinic acid in, II, 214  
   insoluble brominated glycerides in, II, 219  
   iodine values for, II, 217  
   medicinal, II, 216  
   mixed fatty acids from, II, 215  
   refraction of, II, 217  
   Reichert-Meissl value for, II, 218  
   saponification value for, II, 217  
   skate-liver oil as a substitute for, II, 220  
   specific gravity of, II, 217  
   substitutes for, II, 216  
   unsaponifiable matter in, II, 219  
 Cod-liver oil, varieties of, II, 214  
 Coerulein, III, 547, 557; V, 299, 302, 453, 463, 570  
   (in paste) detection of, V, 447  
   S, SW, V, 299, 302  
     detection of, V, 445  
 Coerulignone, III, 340  
 Coffalic acid, VI, 646  
 Coffee, VI, 642; IX, 530  
   adulterants, composition of, VI, 675  
   alkaloids in, VI, 646  
   analyses of, VI, 675  
   aqueous extract of, VI, 658  
   ash of, VI, 653  
   beans, adulteration of, VI, 663  
   berries, VI, 651  
     examination of, VI, 651  
     imitation, VI, 663  
     specific gravity of, VI, 670  
   caffeine free, VI, 657; IX, 531  
   caffiol in, IX, 531  
   caffetannic acid, in, VI, 645  
   colouring matters in, V, 658  
   composition, VI, 643  
   detection of chicory in, VI, 671  
     of chlorogenic acid in, IX, 531  
     of starch in, VI, 672  
   estimation of caffeine in, VI, 608, 609, 611, 656; IX, 527  
   of caffetannic acid in, VI, 658  
   of fat in, VI, 656  
   of proteins in, VI, 663  
   of starch in, VI, 663  
   of sugars in, VI, 662  
   extracts, VI, 678; IX, 532  
     detection of benzoic acid in, IX, 282  
     of chicory in, IX, 532  
     tinctorial power of, VI, 676  
   fat of, VI, 647  
   ground, adulteration of, VI, 670  
     analysis of, VI, 653  
   mixtures, estimation of coffee in, VI, 662  
   Mogdad, VI, 665  
   moisture in, IX, 530  
   nitrogenous constituents of, VI, 648  
   parchment, VI, 643  
   roasting of, VI, 648  
   substitutes for, VI, 663; IX, 531  
   sugar in, VI, 643  
   toxicity of, IX, 531  
   volatile oil of, VI, 650  
 Cognac oil, IV, 440  
 Coke, formation of, in dry distillation, III, 14  
   residual estimation of, in bitumen, III, 72  
 Coke-oven tar, III, 33  
 Colchic acid, VII, 6, 8  
 Colchicine, VII, 7  
 Colchicine, VII, 4; IX, 534  
   bromo-derivatives of, IX, 534  
   derivatives, activity of, IX, 534  
   estimation of, VII, 8  
   morphine and codeine, distinction between, VII, 5  
   preparation of, VII, 9  
   salicylate, III, 492  
 Colchicinic acid. See *Colchic acid*.

- Colchicum alkaloids, VII, 4; IX, 534  
 assay of, VII, 8  
 toxicology of, VII, 11
- Colchisal, III, 492
- Colden's liquid beef, IX, 614
- Collagen, VIII, 91, 582, 585
- Collidines, VI, 129, 144
- Colocynth bitter, VII, 157  
 pulp, VII, 159
- Colocynthein, VII, 158
- Colocynthin, VII, 157
- Colophene, IV, 187  
 production of, from pinene, IV, 180
- Colophonates, IV, 32
- Colophonia elemi, IV, 96
- Colophony, IV, 12, 15, 21  
 abietic acid in, IV, 22  
 acetyl value of, IV, 28  
 acid value of, IV, 12, 25, 26  
 adulteration of, IV, 24  
 storax with, III, 465  
 composition of, IV, 21  
 constants of, IV, 25  
 detection of, IV, 28  
 in beeswax, II, 256  
 in copaiba balsam, IV, 90  
 in oils, II, 76  
 in paper, I, 477  
 in shellac, IV, 69  
 Tolu balsam, III, 460  
 dry distillation of, IV, 36  
 effect of, on amber, IV, 20  
 ester number of, IV, 12, 26  
 esters of, IV, 36  
 estimation of, IV, 29  
 in oils, II, 76  
 in paper, I, 477  
 in printing ink, IX, 459  
 in soap, IV, 30  
 iodine value of, IV, 12, 28  
 melting point of, IV, 24  
 and petroleum, detection of a mixture of  
 in oil of cassia, III, 445  
 properties of, IV, 24  
 saponification number of, IV, 26  
 solubility of, IV, 24  
 specific gravity of, IV, 24  
 unsaponifiable matter in, IV, 27  
 uses of, IV, 23
- Colostrum, VIII, 139
- Colouring matters, V, 115  
 absorption, spectra of, V, 435  
 acridine, V, 358, 360, 366  
 from amino-acetanilide, V, 200  
 amino azo, V, 138, 141  
 analysis of, V, 435; IX, 419  
 animal fibres, identification of, V, 489  
 azine, V, 316, 328, 461, 462  
 azo-, V, 133, 462, 465, 466  
 action of concentrated sulphuric acid on,  
 V, 204  
 reducing agents on, V, 204  
 analytical reactions of, V, 203, 204  
 bases produced by the reduction of, V, 205  
 detection of, V, 445
- Colouring matters, azo-, estimation of, V, 480  
 azoxy, V, 132  
 benzidine, V, 176  
 black, V, 532, 558  
 in animal fibres, V, 496, 509  
 blue, V, 455, 588  
 in animal fibres, V, 494, 504  
 on cotton, V, 526  
 on silk, V, 515  
 in vat dyes, V, 537  
 brown, V, 610  
 in animal fibres, V, 496, 508  
 on cotton, V, 530  
 from vat dyes, V, 538  
 chemical investigation of, V, 443  
 nature of, V, 116  
 classification, V, 119, 267, 444  
 coal-tar. See *Coal-tar dyes*.  
 commercial, examination of, V, 475  
 compound shades, on animal fibres, detection  
 of, V, 510  
 detection of, in tea, VI, 630  
 diaminoazoxy-, V, 198  
 diamino-phenyl-tolyl, V, 190  
 diamino-stilbene, V, 196  
 diaminotriphenylmethane, V, 239  
 di-o-chlor-benzidine, V, 196  
 diphenylmethane, V, 231  
 estimation of, V, 478  
 by their absorption, spectra, V, 438  
 Knecht's process, V, 478  
 of small quantities of, IX, 419  
 examination of, by capillary separation, V,  
 441  
 with tintometers, V, 439  
 fastness of, V, 482; IX, 419  
 fluoran, V, 286, 302  
 fluorescence of, V, 438  
 in foods, V, 623, 625; IX, 449  
 detection of, V, 648  
 effect of solvents on, IX, 452  
 separation of, IX, 449, 453  
 foreign, V, 478  
 green, V, 453, 570  
 in animal fibres, V, 495, 506  
 on cotton, V, 528  
 on silk, V, 515  
 from vat dyes, V, 538  
 Green's analysis for, V, 460  
 grey, V, 532, 558  
 in animal fibres, V, 496, 509  
 from vat-dyes V, 538  
 hydrazine, V, 462  
 hydroxy-azo, V, 135, 139, 142  
 hydroxyketone, V, 206  
 from indamines, V, 310, 314  
 from indophenols, V, 310, 314  
 in meat products, detection of, VIII, 382  
 mechanical mixtures of, V, 443  
 mixed, separation of, V, 475  
 of natural origin, V, 383, 625  
 nitro-, V, 120, 122, 462, 465, 466, 473  
 detection of, V, 445  
 nitroso-, V, 129, 462, 465, 466  
 iso-nitroso, V, 129

- Colouring matters, orange, v, 576  
     in animal fibres, v, 492, 498  
     on cotton, v, 520  
     on silk, v, 513  
     from vat dyes, v, 535  
     orange-red, v, 456  
 oxazine, v, 341, 346, 461, 462  
 phthaleins, v, 461, 462  
 physical investigation of, v, 435  
 poisonous metals in, v, 478  
 polyazo-, v, 176  
 purple, in animal fibres, v, 493, 502  
     on cotton, v, 524  
     in vat dyes, v, 537  
 pyrazolone, v, 133  
 pyrone, v, 286, 302  
 quinoline, v, 358, 366  
 red, v, 448, 540  
     in animal fibres, v, 493, 500  
     on cotton, v, 522  
     of natural origin, v, 421  
     on silk, v, 514  
     in vat dyes, v, 536  
 redwood, v, 431  
 relation of, to fibres, v, 117  
 Rota's analysis for, v, 464  
 on silk, detection of, v, 511  
 sulphide, v, 462  
 sulphonated azo, v, 136  
 sulphur, v, 370, 374  
     classification of, v, 375  
     prefixes for, v, 380  
 tetramethyldiamino-benzophenone, v, 255  
 tetrazo, v, 133, 160, 165  
 thiasine, v, 353, 356, 461, 462  
 thiazole, v, 370  
 from tolidine, v, 190  
 triaminotriphenylmethane, v, 244  
 triphenylmethane, v, 231, 461  
     properties of, v, 265  
 on vegetable fibres, identification of, v, 516  
 violet, v, 454, 604  
     in animal fibres, v, 493, 502  
     in vat dyes, v, 537  
     on cotton, v, 524  
     on silk, v, 515  
 Weingartner's tables for the recognition of, v, 444  
 Wilt's tables for the examination of, v, 447  
 xanthone, v, 286, 302  
 yellow, v, 456, 576  
     in animal fibres, v, 492, 498  
     in vat dyes, v, 535  
     natural, v, 408  
     on cotton, v, 520  
     on silk, v, 513
- Colours, developed, v, 202  
     ingrain, v, 118, 202, 372  
 Columbamine, vi, 575  
 Columbia fast scarlet, v, 554  
     green, v, 572  
     violet R, v, 608  
 Columbian bark, vi, 480  
 Columbic acid, vi, 577  
 Columbin, vi, 576
- Colza oil. See *Rape oil*.  
 Colzarine oil, iii, 118  
 Combustion, estimation of carbon and hydrogen  
     by means of, i, 57  
 Compound ethers. See *Esters*.  
 Conalbumin, viii, 91, 433  
 Conchairamidine, vi, 500, 546  
 Conchairamine, vi, 500, 546  
 Conchiolin, viii, 91, 672  
 Concusconine, vi, 500, 546  
 Condensed milk. See *Milk, condensed*.  
 Condensers, i, 18  
 Confectioners' glucose, United States standard  
     of purity of, i, 378  
 Confectionery, colouring matters in, v, 657  
 Conglutin, viii, 111, 112  
     leucine from, vii, 229  
 Congo G, v, 178  
     P, v, 178  
     brown G, v, 180, 612  
     R, v, 180, 612  
     V, NBR, v, 612  
 corinth, v, 542  
     B, v, 192, 544, 606  
     G, v, 178, 544  
 orange, v, 582  
     R, v, 192  
 pure blue, v, 188  
 red, v, 177, 178, 451, 466, 540  
     4 R, v, 194, 547  
     brilliant. See under *Brilliant*.  
 violet, v, 178, 606  
 yellow, v, 178  
 Conhydrine, vi, 212, 214  
     hydrochloride, tests for, vi, 219  
     tests for, vi, 218, 220  
 pseudo-Conhydrine, vi, 212, 215  
     hydrochloride, tests for, vi, 219  
     tests for, vi, 218, 220  
 Coniceine, tests for, vi, 218, 220  
 Coniceines, vi, 215  
 Coniferin, vii, 99  
 Conifers, glucosides of, vii, 99  
 Coniine, vi, 211  
     assay of, vi, 221; ix, 481  
     hydrochloride, tests for, vi, 219  
     methonitrite, ix, 481  
     poisoning by, vi, 216  
     salts of, vi, 213  
     tests for, vi, 217  
 Coniinium nitrite, ix, 481  
 Conium alkaloids, vi, 211; ix, 481  
     separation of, vi, 221  
     oil, iv, 440  
 Conjugated proteins. See under *Proteins*.  
 Conquinamine, vi, 499, 537  
 Conquinine. See *Quinidine*.  
 Convolvulin, vii, 130  
 Convolvulinolic acid, vii, 130  
 Coomassie navy blue R, v, 594  
     wool black 4BS, v, 564  
 Copaiba, adulterated, ix, 313  
     African, ix, 313  
     balsam, iv, 82  
     adulterants of, iv, 88

- Copaiba**, detection of Guijun balsam in, IX, 315  
 oil, IV, 84; V, 440; IX, 314, 315  
 resin, IV, 85, 87; IX, 313
- Copal**, IV, 15; IX, 310  
 angola, IV, 52  
 benin, IX, 310  
 benguela, IV, 51  
 Manila, IV, 52; IX, 310  
 pebble, IV, 52  
 Sierra Leone, IV, 52  
 Zanzibar, IV, 51
- Copalresenes**, IV, 6
- Copala**, IV, 12, 47; IX, 310  
 adulterants of, IV, 51  
 composition of, IV, 48, 50  
 constants for, IV, 55; IX, 310  
 hardness of, IV, 53  
 melting point of, IV, 54; IX, 310  
 properties of, IV, 51  
 solubility of, IV, 54  
 specific gravity, IV, 53  
 uses of, IV, 51  
 varieties of, IV, 48, 50; IX, 310
- Copper acetates**. See *Cupric acetates*.  
 amino-caproate, VII, 230  
 arsenite, use of, as a colouring matter for  
 sweets, I, 358  
 butyrate, I, 523  
 carbonyl-ferricyanide, VII, 532  
 detection of, in cheese, VIII, 258  
 in olive oil, II, 111  
 in organic substances, I, 75  
 estimation of, in cyanide solutions, VII, 495  
 sulphate, detection of, in flour, I, 457
- Coralline**, v, 261, 462  
 aurin R, v, 274  
 red, v, 262, 274  
 yellow, v, 262
- Cordials**, colouring matters in, v, 655
- Cordite**, application of Abel test to, III, 599  
 composition of, III, 593  
 test for mercury in, III, 609  
 Waltham Abbey silvered vessel test for, III,  
 614
- Coreine**, v, 346  
 AB, AR, v, 346  
 RR, v, 346
- Coriander oil**, IX, 244, 249, 250, 332, 440
- Corioflavine GG**, G, R, RR, v, 368
- Cork bark**, reactions of, v, 44
- Corn oil**. See *Maise oil*.
- Cornin**, VIII, 91, 673
- Cornmeal**, composition of, I, 464
- Corpuscles**, red, VIII, 498
- Corridine**, VI, 129
- Corvan black B**, v, 568
- Corydaline**, oxidation of, VI, 205
- Corylin**, VIII, 109
- Cosaprine**, III, 397
- Cosmin**, III, 503
- Costus oil**, IV, 441
- Cotarnine**, constitution of VI, 358  
 estimation of, in the presence of sugar, VI, 433
- Cotton blue** v, 252, 254, 284  
 3 B, v, 252
- Cotton blue**, R, v, 341  
 for cotton, v, 341  
 bordeaux, v, 182  
 brown R, A, N, v, 612  
 fibres, microscopic appearance of, in paper,  
 I, 474  
 identification of dyes on, v, 516  
 materials, estimation of small quantities of  
 wool in, IX, 623  
 oil stearine, II, 181  
 orange G, v, 158  
 red, v, 192  
 rhodine BS, v, 302  
 scarlet, v, 168, 200  
 3B, v, 550  
 yellow G, v, 200, 580  
 R, v, 140
- Cottonseed oil**, II, 70, 132; IX, 135  
 blown, II, 362, 365, 368  
 colour tests for, II, 135  
 composition of, II, 13  
 crude, properties of, II, 132  
 detection of, in arachis oil, II, 101  
 by Halphen's test, II, 300; IX, 135  
 in olive oil, II, 117  
 in other oils, II, 134  
 by the nitric acid colour test, II, 41  
 in rape oil, II, 130  
 in sesame oil, II, 146  
 in the fatty acids from the lead soaps  
 soluble in ether, II, 138  
 effect of temperature on the viscosity of,  
 III, 148  
 group of oils, II, 65, 70, 131  
 Halphen's colour test for, II, 135; IX, 135  
 liability of, to inflame spontaneously, II,  
 513  
 melting point of the mixed fatty acids  
 from, II, 133  
 mixed fatty acids from, II, 133, 134  
 nitric acid test for, II, 138  
 and rape oil, distinction between, II, 370  
 refined, properties of, II, 133  
 silver nitrate test for, II, 136  
 and stearine, detection of, in tallow, II, 211  
 use of, to replace olive oil, II, 112  
 stearin, II, 133, 134
- Coumaric acids**, III, 447
- p*-Coumaric acid, occurrence of, in resins, IV, 3
- Coumarin**, III, 447  
 detection of, in vanilla essence, III, 522; IX,  
 306  
 estimation of, IX, 294  
 and vanillin, separation of, III, 519
- Coupler's blue**, v, 327
- Crampfish oil**, II, 223
- Cream**, VIII, 139, 179  
 aldehyde figure for, IX, 599  
 analysis of, VIII, 187  
 clotted, VIII, 185  
 detection of agar-agar in, VIII, 193  
 of benzoic acid in, VIII, 190  
 of boron compounds in, VIII, 190  
 of calcium saccharate in, VIII, 193  
 of casein in, VIII, 193

- Cream, detection of dried and condensed milks**  
 in, VIII, 193  
 of fluorides in, VIII, 190, 690  
 of formaldehyde in, VIII, 192  
 of formic acid in, VIII, 191  
 of gelatin in, VIII, 193  
 of hexamethylene tetramine in, VIII, 192  
 of homogenisation in, VIII, 194  
 of hydrogen peroxide in, VIII, 191  
 of mystin in, VIII, 192  
 of  $\alpha$ - and  $\beta$ -naphthols in, VIII, 192  
 of pectoses in, VIII, 194  
 of salicylic acid in, VIII, 190  
 of starch in, VIII, 194  
 estimation of boron compounds in, VIII, 194  
 of fat in, VIII, 151  
   by the Babcock method, VIII, 187  
   by the Gerber process, VIII, 187; IX, 599  
   by the Gottlieb process, VIII, 188  
   by the Mats-Weibull method, VIII, 188  
 of nitrogen in, VIII, 190  
 of salicylic acid in, III, 485; VIII, 195  
 of total solids in, VIII, 189  
 preservatives in, VIII, 190  
   regulations for, IX, 597  
 separation of, VIII, 180  
 thickening agents in, VIII, 193
- Cream of tartar**, I, 552, 543; IX, 103  
 acidity of, IX, 103  
 adulteration of, I, 543  
 commercial, assay of, I, 548
- Creatine**, VII, 308; VIII, 287  
 estimation of, IX, 567, 610  
   in meat extracts, VIII, 410  
 preparation of, from urine, IX, 565
- Creatinine**, VII, 311; VIII, 287  
 and creatine, distinction between, VII, 310  
 estimation of, VII, 315; IX, 566, 610  
   in meat extracts, VIII, 410  
 Jaffé reaction for, VIII, 410  
 preparation of, from urine, IX, 565  
 salts of, VII, 312
- Creatinine-zinc chloride**, VII, 312
- Creolin**, III, 332  
 analysis of, III, 333
- Creosol**, III, 337, 346  
 methyl ether, III, 346
- Creosote**, III, 346  
 antiseptic properties of, IX, 276  
 blast-furnace tar, III, 362  
   detection of, in wood-tar creosote, III, 362  
 flash and fire point determinations, III, 378  
 oil, III, 250  
   analysis of, III, 353  
   assay of, III, 371, 374; IX, 275  
   coal-tar, III, 365  
     analysis of, III, 371  
     assay of, III, 374  
     composition of, III, 366  
     when extracted from creosoted timber,  
     III, 369  
   composition of, III, 352  
   determination of moisture in, III, 378, 381,  
   384  
   distillation of, III, 375, 379
- Creosote, oil estimation of basic constituents in**,  
 III, 377  
   of naphthalene in, III, 374  
   of tar acids in, III, 375, 379, 384  
   extracted from creosoted timber, analysis  
   of, III, 389  
   grades of, for creosoting timber, III, 385  
   melting point determination, III, 378  
   oak, III, 353  
   preservative properties of, III, 371  
   specific gravity determination, III, 378  
   sulphonation test for, III, 384  
   technical examination of, III, 377  
   water-gas tar, III, 371
- oils**, III, 365  
   application of, III, 367, 371  
   coke test for, IX, 276
- shale-oil**, III, 365
- sheep dips, analysis of**, III, 318  
   estimation of light oils in, III, 328  
     of naphthalene in, III, 328  
     of phenols in, III, 321  
     of rosin acids, gravimetrically, III, 325  
     volumetrically, III, 326  
   of soda and pyridine bases in, III,  
   318
- foreign oils and creosotes in**, III, 328
- wood-tar**, III, 347  
 adulterations of, III, 358  
 assay of, III, 355  
 commercial, examination of samples of,  
 III, 357  
 composition of, III, 349  
 detection of blast-furnace tar creosote in,  
 III, 362  
   of phenol in, III, 355  
 estimation of guaiacol in, III, 355  
 glycerol test for, III, 360  
 optical activity of, III, 358  
 phenol and cresylic acid, differentiation  
 between, III, 358  
 separation of phenaloid constituents in,  
 III, 351  
 specifications of, for preserving timber,  
 III, 367  
 tests for, III, 348, 358
- Creosotum**. See *Creosols, wood-tar*.
- Cresatols**, III, 498
- o-Cresol**, III, 312, 313  
 estimation of, IX, 272
- p-Cresol**, III, 312, 313  
 estimation of, IX, 272
- m-Cresol**, III, 312  
 estimation of, IX, 273  
   in a mixture of cresols, III, 314; IX, 273  
   by Raschig's method, IX, 273  
 separation of, from o- and p-cresol, III,  
 313
- Cresol dips**. See *Cresylic acid dips*.
- Cresoline**, III, 332
- o-, m- and p-Cresols, colour reactions of, with chlo-  
 roform and alkali**, III, 297  
 distinctions between, III, 312, 313  
 formation of, III, 311  
 properties of, III, 312



- Cresotic acid, in commercial salicylic acid, III, 472  
     acids, III, 508  
     physiological actions of III, 509  
 Cresotin yellow G, v, 582  
 Cress seed oil, II, 70, 139  
 Cresylic acid, antiseptic and disinfectant properties of, III, 317, 331  
     from coal-tar, III, 315  
     commercial, distillation of, III, 317  
     detection of phenol in, III, 317  
     and phenol, differences between, III, 316  
     sheep dips, analysis of, III, 329  
     detection of, excess of alkali in, III, 331  
     estimation of, phenols in, III, 330  
     rosin acids in, III, 330  
     soap in, III, 331  
     soda and pyridine bases in, III, 329  
     water in, III, 329  
     and wood-tar creosote, distinction between, III, 358  
 Cresyl-sulphuric acid, occurrence of, III, 399  
 Crimson, alkali, v, 552  
 Crocein B, v, 161, 162, 168  
     3 B, v, 168  
     3 BX, v, 152, 544  
     Orange, v, 136, 137, 139, 142, 578  
     scarlet, v, 160  
     3 B, v, 160, 162, 168, 451, 544  
     7 B, v, 160, 162, 170, 540  
     extra, v, 451  
 Crocetin, v, 418  
 Crocin, v, 418  
 Cross dye black, v, 560  
     drab, v, 612  
 Croton oil, II, 71, 172; IX, 146  
 Crumpsall direct fast brown O, v, 612  
     yellow, v, 158  
     YYFD, v, 582  
 Crurin, VI, 152  
 Crusocreatinine, VII, 317  
 Cryogene brown, v, 380  
 Cryptopine, VI, 354, 364, 396  
 Chrysoldine, detection of, v, 445  
 Crystal Ponceau, 6 R, v, 148  
     scarlet, v, 544  
     violet, v, 234, 257, 274, 461  
     6 B, v, 606  
     7 B extra, v, 274  
     5 BO, v, 257, 274  
     C, v, 274  
     detection of, v, 445  
     O, v, 257, 274  
 $\alpha$ - and  $\beta$ -Crystallins, VIII, 91  
 Crystallose, III, 429  
 Cubeb oil, IV, 249, 250, 333, 441; IX, 358  
 Cubeb-camphor, IV, 333; IX, 343  
 Cubebene, IV, 186  
 Cubeol, IV, 287  
 Cudbear, v, 428, 635, 636, 637  
 Culilaban oil, IV, 441  
 Culture yeasts. See *Yeasts, culture*.  
 pseudo-Cumene, behaviour of with benzal chloride, III, 280  
 Cumidine red, v, 548  
 Cumidines, VI, 73  
 Cumin oil, IV, 244, 334, 441  
     essential, I, 255  
     methoxyl number, IV, 242  
 Cuminol, estimation of, in cumin oil, IV, 334  
 Cummin oil. See *Cumin oil*.  
 Cuprea bark, VI, 480; IX, 514  
 Cupreine, VI, 499, 548  
     detection of, in quinine sulphate, VI, 522  
     and homoquinine, distinction between, VI, 550  
     and quinine, distinction between, VI, 514  
     salts of, VI, 549  
 Cupric acetates, I, 513  
     benzoate, III, 415  
     oleate, II, 412  
 Cuprous cyanide, VII, 476  
     oxide, estimation of, in Allihn's analysis of  
         sugars by direct weighing, I, 325  
         electrolytic deposition, I, 323  
         reduction in hydrogen, I, 323  
         titration with permanganate, I, 324  
     thiocyanate, VII, 547  
     xanthate, I, 241  
 Curare, VI, 474  
     alkaloids of, VI, 474  
     bamboo, VI, 475  
     calabassen or gourd, VI, 476  
     pot, VI, 477  
 Curarine, VI, 476  
 Curcas oil, II, 71, 173  
 Curcuma-arrowroot starch, I, 412, 415  
 Curcumin, v, 138, 414, 459  
     S, v, 132, 580  
     W, v, 578  
 Curcuphenin, v, 582  
 Curine, VI, 475  
 Cutch. See *Catechu*.  
 Cutch BG., immedial, v, 620  
     R pyrogene, v, 618  
 Catches, reactions of, v, 45  
 Cutin, estimation of, in crude fibre, I, 437  
 Cutocelluloses, I, 434  
 Cutose, I, 434  
 Cyanamide, VII, 556  
     detection of, in commercial cyanide, VII, 488  
     salts, IX, 589  
 Cyanamides, VII, 557  
     estimation of, VII, 558  
 Cyananthrol R, v, 600  
 Cyanates, formation of, VII, 535  
     metallic, VII, 536  
     detection of, VII, 539  
     estimation of, VII, 540  
 Cyanhæmochromogen, VIII, 552  
 Cyanhæmoglobin, VIII, 537  
 Cyanic acid, VII, 535  
     polymers of, VII, 541  
 Cyanide, commercial, analysis of, VII, 484  
     detection of, cyanamide in, VII, 488  
     cyanates in, VII, 539  
     poisoning, antidotes for, VII, 467, 470  
     process for gold extraction, VII, 499  
     solutions, estimation of, gold in, VII, 493  
     metals in, VII, 493  
     reducing power of, VII, 495  
     silver in, VII, 494

- Di-*p*-amino-diphenyl. See *Benzidine*.  
 Diaminogene blue G, v, 592  
     NA, v, 600  
     extra, v, 592  
 1:5-Diaminonaphthalene-3:7-disulphonic acid, vi, 124  
 1:8-Diaminonaphthalene-3:6-disulphonic acid, vi, 124  
 1:4-Diaminonaphthalene-6-sulphonic acid, vi, 124  
 Diaminophenols, vi, 105  
 Diaminotoluenes. See *Tolylene-diamines*.  
 Diaminotriphenylmethane dyestuffs. See under *Colouring matters*.  
 Diamogene blue G, v, 592  
     sky blue N, v, 600  
 Diamond black, v, 172, 558  
     2 B, v, 564  
     flavin G, v, 156  
     green, v, 241, 278, 570  
     red G, v, 552  
     yellow, v, 466  
     yellow G, v, 154, 580  
     R, v, 154  
 Dianil black, v, 188  
     brown 3 G, v, 616  
     dark blue 3 R, v, 598  
     fast scarlet 6 BS, v, 552  
     yellow 2 R, v, 584  
 Dianisidine blue, v, 88 1  
 Dianol black brown, v, 612, 614  
     cotton brown N, v, 618  
     olive, v, 614  
     red 2 B, v, 196  
 Dianthin, v, 548  
     B, v, 296  
     G, v, 304  
 Dianthracene, iii, 263  
 Diaptherin, vi, 160, 403  
 Diaphtol, iii, 403  
 Diastase, viii, 3  
     Lintner value of, vii, 3  
     method for the estimation of starch, i, 420  
     preparation of, for the estimation of starch, i, 421  
     in yeast, i, 212  
 Diastatic power of enzymes, determination of, viii, 3, 689  
     of flour, estimation of, i, 455  
*p*-Diazobenzene-sulphonic acid, v, 134  
 Diazo black 2 B, v, 562  
     R, v, 560  
     brilliant black B, v, 560  
     scarlet PR extra, v, 556  
     fast black MG, v, 562  
     indigo blue, v, 596  
     marine blue G, v, 602  
 Dibenzylanthracene, behaviour of, with benzal chloride, iii, 280  
 Dibenzolyaconine, vi, 264  
 $\alpha$ - $\alpha'$ -Dibromocamphor, iv, 207  
 $\alpha$ - $\beta$ -Dibromocamphor, iv, 209  
 $\alpha$ - $\pi$ -Dibromocamphor, iv, 210  
 Dibromo-dinitro-fluorescein, v, 296  
 Dibromogallic acid, iii, 535  
 3:5-Dibromopyridine, vi, 133  
 $\alpha\alpha$ -Dicamphorarsenic acid, iv, 208  
 Dichloranthracene, effect of solvents on, iii, 274  
 $\beta$ -Dichlorethane. See *Ethylidene chloride*.  
 Dichlormethane. See *Methylene dichloride*.  
 Dicinchonine, vi, 500, 545  
 Dicyanamide, estimation of, vii, 558  
*p*-Diethoxyethenyldiphenylamidin, vi, 104  
 Diethylamine, vi, 20  
     as a putrefaction product, vii, 352  
 Diethylaniline, vi, 88, 91, 95  
 Diethylene-diamine. See *Piperazine*.  
 Diethylhydrazines, vi, 30  
 Diethyl- $\alpha$ -naphthylamine, vi, 116  
 Digallic acid, v, 7, 16  
 Digests of proteins. See *Protein digests*.  
 Digitaligenin, vii, 117  
 Digitalin, vii, 116  
     colour reactions of, vii, 120  
     commercial, vii, 119  
 Digitalinum Germanicum, ix, 547  
 Digitalis, ix, 546  
     glucosides of, vii, 116  
     estimation of, vii, 119  
     physiological action of, vii, 118  
     tincture, test for, ix, 546  
 Digitonin, vii, 118  
     reactions of, ix, 546  
 Digitonin-cholesteride, ii, 481  
 Digitoxigenin, vii, 118  
 Digitoxin, vii, 117  
     colour reactions of, vii, 120  
     and gitalin, separation of, ix, 547  
 Digitoxose, vii, 117  
 Diglyceryl triphthalate, iii, 544  
 Dihydroacridine, vi, 164  
 Dihydroquinoline, vi, 155  
 Dihydrosparteine, vi, 234  
*o*-Dihydroxy-anthraquinone. See *Alizarin*.  
*m*-Dihydroxy-azobenzene, v, 135  
*m*-Dihydroxybenzene. See *Resorcinol*.  
*o*-Dihydroxybenzene. See *Catechol*.  
*p*-Dihydroxybenzene. See *Quinol*.  
 Dihydroxybenzenes, iii, 335  
     homologues of, iii, 337  
 Dihydroxybenzoic acids, isomeric, iii, 511  
 2:8-Dihydroxy-1:7-dimethylpurine, ix, 526  
 2:8-Dihydroxy-1:7:9-trimethyl-purine, ix, 526  
 2:6-Diiodo-phenol-4-sulphonic acid, iii, 398  
 Diiodo-salicylic acid, iii, 501  
 Dika fat, detection of, as a substitute for cacao butter, ii, 179  
 Dill-apiol, iv, 336  
 Dill oil, iv, 249, 335, 441  
 Dimethyl-acetal, i, 268  
 Dimethylamine, vi, 11, 14  
     and ammonia, separation and estimation of, vi, 18  
     as a putrefaction product, vii, 352  
 Dimethylaminoazobenzene, v, 135, 456  
 Dimethylaniline, vi, 89  
     commercial, vi, 91  
     orange, v, 138  
     test for formaldehyde, i, 259  
 Dimethylantracene, iii, 265  
 Dimethylbenzenes. See *Xylenes*.

- Dimethylcolchic acid, VII, 6, 8  
 Dimethyl-*p*-diamino-benzene, v, 206  
 Dimethylhomocatecholates, III, 346  
 Dimethylhydrazines, VI, 30  
 Dimethyl-ketone. See *Acetone*.  
 Dimethylnaphthalenes, III, 251  
 Dimethylnaphthylamines, VI, 116  
 Dimethylnitrosamine, VI, 14  
 Dimethylphenosafranine, v, 334  
 Dimethyl-*p*-phenylene-diamine, VI, 107  
 Dimethylpyridines, VI, 143  
 2:5 Dimethylpyrrole, VI, 150  
 Dimethylsarcosine. See *Betaine*.  
 Dimethylthiophen, III, 211  
 1:3 Dimethylxanthine. See *Theophylline*.  
 3:7 Dimethylxanthine. See *Theobromine*.  
 Dinaphthylamines, VI, 116  
 Dinaphthyls, reaction of, with metallic chlorides, III, 277  
 Dinicotinic acid, VI, 147  
 Dinitromonochlorhydrin, III, 575  
 2:4-Dinitro- $\alpha$ -naphthol, v, 125  
 2:4 Dinitro- $\alpha$ -naphthol-sulphonic acid and its salts, v, 127  
 Dinitroglycerin, III, 574  
 Dinitrophenol, estimation of, in picric acid, III, 583  
 Dinitroresorcinol, v, 130, 131, 570  
 detection of, v, 447  
 Dinitroso-piperazine, VII, 201  
 Dionine, VI, 368, 390; IX, 500  
 Diosphenol, IV, 255, 298  
 Dioxin, v, 130, 131, 463, 466, 570, 612  
 2,6-Dioxypurine. See *Xanthine*.  
 Dioxysparteine, VI, 234  
 Dipalmitin, II, 397, 398  
 Dipentene, IV, 172  
 bromides, IV, 174  
 dihydrochloride, IV, 173, 182  
 nitrolamines from IV, 175, 176  
 Dipentenes. See *Terpenes*.  
 Diphenyl, III, 266, 268  
 behaviour of, with chromic acid, III, 278  
 black base I, v, 566  
 catechin, G, v, 174  
 chrysoin R R., v, 174  
 compound of, with picric acid, III, 275  
 fast brown G, v, 174  
 orange R. R., v, 139  
 reactions of, with metallic chlorides, III, 277  
 Diphenylamine, VI, 88, 95, 205  
 blue, v, 250, 455, 463  
 detection of, v, 447  
 spirit soluble v, 274  
 orange v, 138, 145  
 reaction of, with nitric acid, VI, 96  
 yellow v, 141, 145  
 Diphenylaniline, VI, 88, 97  
 Diphenylene-imide. See *Carbasol*.  
 Diphenylmethane, III, 266, 268; v, 231  
 behaviour of, with benzal chloride, III, 280  
 colouring matters. See under *Colouring matters*.  
 Dipicolinic acid, VI, 147  
 Dipyridine, VI, 134  
 4:4'-( $\gamma$ )-Dipyridyl, VI, 133  
 Diquinicine, VI, 500, 545  
 Direct black FF extra, v, 568  
 blue B, v, 186  
 R, v, 194  
 brown 5 G, v, 620  
 J, v, 168  
 brown-yellowish 3 GO, v, 618  
 cotton dyestuffs, v, 176  
 dark brown M, v, 618  
 deep black E extra, v, 562  
 G, v, 560  
 fast scarlet R, v, 552  
 grey, v, 314  
 B, v, 194  
 R, v, 180  
 red, v, 190  
 B, v, 178  
 violet, v, 256  
 N, v, 610  
 yellow, v, 190  
 G, v, 132  
 R, v, 582  
 Disaccharides, properties of, I, 286  
 table showing the origin and properties of the more important, I, 288  
 Disalicylide, III, 499  
 Disinfecting liquids, phenolic, III, 331  
 analysis of, III, 333  
 powders, phenolic, III, 308  
 Dispersion, I, 22  
 Distillation, I, 18  
 destructive, III, 11, 15  
 fractional, I, 18  
 under reduced pressure, I, 21  
 Ditaine, VI, 547  
 Ditamine, VI, 547  
 Diterebentyl, IV, 39  
 Diterpenes, IV, 163, 187  
 Diterpilene, IV, 187  
 Dithio-diamino-dilactic acid. See *Cystin*.  
 Dithion, III, 501  
 Di-thio-salicylic acid and its salts, III, 501  
 Diuretin, III, 491; VI, 594  
 Divi-divi, v, 35  
 analysis of, v, 67, 102  
 decomposition products of, v, 55  
 reactions of, v, 42, 50  
 Doebner's violet, v, 239  
 Doegling oil. See *Sperm oil, Arctic*.  
 Dog-fennel oil, IV, 441  
 Dog fish oil, II, 223  
 Dolphin oil, II, 242  
 Domingo alizarin black B, v, 566  
 brown B, v, 620  
 blue-black LW, v, 566  
 chrome black FF, v, 566  
 yellow G, v, 586  
 Double brilliant scarlet G, 3 R, v, 152  
 green, v, 259  
 refraction, I, 41  
 scarlet, v, 170  
 extra S, v, 152  
 Doughing test for flour, I, 454  
 Dracalban, IV, 6  
 Dracoresene, IV, 6

- Dracoresinotannol, IV, 4  
 Dragendorff's reagent for alkaloids, VI, 190  
 Dragon's blood resin, IV, 12, 15, 62; IX, 310  
 Dreaper's volumetric copper process for tannin assay, V, 70  
 Driers for oils, II, 358  
   resinate. See *Resinate driers*.  
 Drip oils, testing of, IX, 261  
 Dry yeast. See *Yeast, dry*.  
 Drying oils. See *Oils, drying*.  
 Duatol black 3 B, V, 562  
   bordeaux B, V, 556  
 Duboisine. See *Hyoscyamine*.  
 Dulcine, VI, 104; VII, 302  
 iso-Duridine, VI, 74  
 Durophenine brown, V, 314  
   V, V, 614  
 Dvorkowitsch's method for the estimation of caffeine in tea, VI, 608  
 Dyed fibres. See *Fibres, dyed*.  
 Dyes, V, 115  
   adjective, V, 118  
   classification of, V, 119  
   formulae and lettering of, V, 146, 158  
   substantive, V, 117  
   See also *Colouring matters*.  
 Dynamite, application of the Abel test to, III, 602  
   glycerin. See *Glycerin, dynamite*.  
 Dyslysin, VII, 417

## E

- Earthnut oil. See *Arachis oil*.  
 Easton's syrup, IX, 518  
 Ebler's method for the estimation of hydrazine, VI, 26  
 Eboli blue 2R, V, 598  
   green T, V, 572  
 Ebonite, IV, 143  
   analysis of, IV, 144  
 Ecgonine, VI, 337  
 Echitamine, VI, 547  
 Echitenine, VI, 547  
 Eclipse brown, V, 376  
   B, V, 618  
   green G, V, 574  
   red, V, 192  
   (Geigy), V, 380  
   yellow (Geigy), V, 376  
   3 G, V, 586  
 Edestin, VIII, 109  
 Edible pastes, VIII, 102  
 Eggalbumin, VIII, 433  
   amino-acids formed by the hydrolysis of, VIII, 20  
   estimation of, IX, 621  
   oil, II, 203; VIII, 435  
   powder, analysis of, VIII, 238  
   preparation of crystalline, VIII, 67  
   proteins, VIII, 432  
   -white, VIII, 432  
   hen and duck, distinction, between, IX, 621  
   -yolk, VIII, 435  
   commercial, analysis of, VIII, 436  
   preparation of lecithin from, VII, 281

- Eggs, VIII, 432; IX, 620  
   analysis of, VIII, 448  
   bacteriological examination of, VIII, 450  
   carp's, composition of, VIII, 460  
   cold storage, VIII, 441  
   analysis of, VIII, 446  
   bacteriological examination of, VIII, 451  
   in commerce, VIII, 438, 445  
   composition of, VIII, 439, 446  
   desiccated, VIII, 449  
   estimation of phosphorus in, IX, 611  
   frozen, VIII, 449  
 Eicosylene, IX, 228  
 Eikonogen, VI, 126  
 Elaidic acid, II, 405  
 Elaidin reaction for fixed oils, II, 39  
   test for olive oil, II, 116  
 Elastin, VIII, 91, 631  
 $\alpha$ -Elaterin, VII, 158  
 Elder otto oil, IV, 442  
 Elecampane oil, IV, 442  
 Elemi, IV, 96  
   African, IX, 318  
   Manila, IV, 96; IX, 318  
   oil, IV, 442  
   methoxyl number, IV, 242  
 Elemic acid, IV, 5  
 Ellagic acid, V, 23; IX, 385  
 Ellagitannic acid, V, 7, 23  
 Elliott closed oil-tester, III, 124  
 Eloemargaric acid, II, 155  
 Emerald green, V, 274  
 Emetine, VII, 39; IX, 542  
   salts of, VII, 39; IX, 543  
 Emulsin, VIII, 6  
 Emulsion, separation of liquid and oil in an, II, 6  
 Endotryptase in yeast, I, 212  
 Endoxine, III, 557  
 Engler's closed oil-tester, III, 126  
   viscosimeter, III, 154  
 Enzymes, VIII, 1; IX, 591  
   action of, on glucosides, I, 391  
   classification of, VIII, 1  
   determination of the diastatic power of, VIII, 5  
   estimation of, VIII, 7, 689  
   extraction of, VIII, 1  
   measurement of the activity of, VIII, 2, 7  
   of meat, VIII, 290  
   proteoclastic, VIII, 9, 491  
   measurement of the activity of, VIII, 10  
   in yeast, I, 211  
 Eosin, V, 462, 469, 547  
   A, V, 295, 302, 540  
   B, V, 295, 296  
   10 B, V, 297, 306  
   BB, V, 297  
   BN, V, 296, 302  
   BW, V, 296  
   blue shade, V, 296  
   bluish, V, 304  
   C, V, 295  
   DH, V, 295  
   DHV, V, 296  
   3 G, GGF, V, 295

- Eosin**, GCF, G extra, v, 302  
 J, v, 296, 304  
 3 J, 4 J, v, 295, 302  
 JJP, v, 295  
 KS, v, 295  
 orange, v, 295  
 S, v, 297  
 salmon pink, v, 295  
 scarlet, v, 296, 450  
     B, v, 296, 302  
     BB, v, 296  
 soluble, v, 295  
 spirit, v, 297, 304, 463  
 water soluble, v, 295  
 yellowish, v, 295, 302
- Eosins**, detection of, v, 445, 448  
 reactions of, v, 297
- Epiguanine**, VII, 322, 334
- Erdmann's reagent for alkaloids**, VI, 200
- Erepsin**, VIII, 9
- Ergosterol**, II, 487, 488
- Ergot**, alkaloids of, VII, 16; IX, 537  
 estimation of, VII, 22  
 physiological action of, VII, 22  
 detection of, in flour, I, 458; VII, 23  
 estimation of, in flour, VII, 23
- Ergothioneine**, VII, 20
- Ergotinine**, VII, 16, 20
- Ergotoxine**, VII, 16, 17  
 hydrochloride, VII, 19  
 phosphate, VII, 18  
 physiological action of, VII, 22  
 salts of, VII, 18
- Erica**, v, 374  
 B, v, 546
- Erigeron oil**, IV, 442
- Erio-chrome black**, T, v, 564  
 blue BR, v, 598  
 blue black B, v, 568  
 crown R, v, 616  
 red B, v, 552  
 violet 3 B, v, 608  
 yellow GR, v, 584
- Eriocyanine A**, v, 274
- Eriodictyon oil**, IV, 442
- Erioglaucine**, v, 240, 243  
 A, v, 274, 598
- Erioviridine B**, v, 576
- Bruca sativa seed oil**, II, 69, 121
- Erythrin**, v, 462  
 methyleosin, v, 304
- Erythroextrin**, I, 427  
 and gums, distinction between, I, 439  
 reaction of, with iodine, I, 420, 428  
 and starch, distinction between action of  
     iodine on, I, 420
- Erythroresinotannol**, IV, 4
- Erythrosin**, v, 296, 462, 540, 547; IX, 453  
 B, v, 296, 297, 304, 306  
 BB, v, 297  
 D, v, 296, 304  
 detection of, v, 445  
 G, v, 296, 304  
 separation of, from the other coal-tar colours  
     in meat products, VIII, 383
- Eseramine**, VII, 29
- Eseridine**, VII, 29  
 and eserine, distinction between, VII, 29
- Eserine**, VII, 24; IX, 536  
 blue, VII, 25  
 and eseridine, distinction between, VII, 29  
 salts of, VII, 28
- Esparto fibres**, microscopic appearance of, in  
 paper, I, 475
- Essence of bitter almonds**, III, 426  
 of camphor, IV, 196  
 of peppermint, IV, 375  
 of vanilla, III, 520
- Essences**, estimation of alcohol in, I, 129; IV, 102  
 in sweets, I, 358
- Essential oil of bitter almonds**, I, 255  
 of cinnamon, I, 255  
 of cloves, I, 255  
 of cumin, I, 255  
 of meadow-sweet, I, 255  
 in tea, estimation of, VI, 628
- oils**, IV, 217, 303; IX, 324  
 adulteration of, IV, 245  
 analysis of, IV, 222, 224  
 classification of, IV, 219  
 colouring matters in, IV, 252  
 composition of, IV, 218  
 condensation of the aldehydes of, with  
     acetone, IV, 238  
 constituents of, IV, 252, 431  
 cyclic terpene alcohols occurring in, IV,  
     254, 277  
 detection of alcohol in, IV, 246  
 of chloroform in, IV, 247  
 of citral in, IV, 271  
 of cymene in, IV, 165  
 of esters in, IX, 330  
 of ethyl citrate in, IX, 331  
 of geraniol in, IV, 260  
 of glyceryl acetate in, IX, 332  
 of methyl anthranilate in, IV, 363  
 of oil of turpentine in, IV, 247  
 of phenols in, IV, 226  
 of sulphur compounds in, IV, 224  
 of terpinyl acetate in, IX, 331
- determination of the carbonyl numbers of,  
 IV, 236  
 of the iodine value of, IV, 239  
 of methoxyl numbers of, IV, 240
- distillation of, IV, 221, 222, 247
- estimation of alcohol in, IV, 247  
 of alcohols in, IV, 227; IX, 328  
     open-chain alcohols in, IV, 264  
 of aldehydes in, IV, 231; IX, 336  
     by Doebner's reaction, IV, 238  
 of cinnamic aldehyde in, IX, 336  
 of citral in, IV, 270; IX, 337  
 of citronellal in, IV, 269, 270  
 of esters in, IV, 230; IX, 333  
 of eugenol in, IV, 294  
 of free acids in, IV, 225  
 of hydrocyanic acid in, IV, 225; IX, 325  
 of ketones in, IV, 231  
 of linalol in, IX, 328  
 of methyl anthranilate in, IV, 363

- Essential oils, estimation of phenols in**, iv, 226;  
     ix, 327  
     of thymol in, ix, 327  
     extraction of, iv, 217  
     formation of semicarbazones from, iv, 235  
     hydrocarbons of, iv, 163; ix, 324  
     ketones in, iv, 189, 231, 256  
     methoxyl numbers of, ix, 240  
     optical activity of, iv, 220, 242  
     oxygenated constituents of, iv, 221  
     pharmacopœial characters of (America),  
         iv, 250  
         (Great Britain), iv, 249  
     phenols and phenolic ethers in, iv, 255, 287  
     properties of, iv, 219, 431  
     refractive indices of, iv, 220, 243; ix, 339  
     sesquiterpene alcohols occurring in, iv,  
         286  
     solubility of, iv, 221, 248  
     specific gravity of, iv, 220, 430, 433  
     sulphur compounds in, iv, 257, 299  
     terpeneless, iv, 429, 430
- Esters**, i, 231  
     estimation of, in essential oils, iv, 230  
     in potable spirits, i, 195  
     in wood naphtha, i, 101  
     examination of, i, 236  
     fruit, saponification of, i, 235  
     hydrolysis of, i, 232  
     mixtures of, i, 233  
         examination of, i, 235  
     in oils and fats, table of saponification equiva-  
         lents and values of, ii, 17  
     physical properties of, i, 231  
     principal boiling points of, i, 234  
         specific gravities of, i, 234  
     production of, i, 231  
     saponification of, i, 231
- Estragol**, iv, 291
- Estrogon oil**, iv, 442
- Ether**. See *Ethyl ether*.  
     extract, estimation of, i, 66  
     nitrous, spirit of. See under *Spirit*.  
     residue, complex, separation of cholesterol  
         from ii, 494  
     spirit of, i, 231
- Ethers, compound**. See *Esters*.  
     nitrous, i, 241
- Ethoxylupanine dihydrobromide**, ix, 482  
     dihydroiodide, ix, 482  
     thiocyanate, ix, 482
- $\beta$ -Ethoxynaphthalene**. See  *$\beta$ -Naphthol ethyl ether*.
- Ethyl acetate, estimation of, in the commercial  
     liquid**, i, 238  
     boiling point of, i, 237  
     commercial, analysis of, i, 237  
         impurities in, i, 237  
     physical properties of, i, 237  
     preparation of, i, 236  
     specific gravity of, i, 237, 238  
     acid violet S 4 B, v, 608
- Ethyl alcohol**, i, 110  
     boiling point of, i, 110  
     British Pharmacopœia standards for, i, 111  
     commercial, examination of, i, 112
- Ethyl alcohol, denatured, detection of pyridine  
     in**, vi, 136  
     estimation of crude benzene in, i, 113  
     detection of, i, 114  
     in commercial chloroform, i, 278, 279  
     chloroform in the presence of large quan-  
         tities of, i, 274  
     in essential oils, iv, 246  
     of ether in, i, 229  
     of methyl alcohol, in the presence of, ix, i  
     of water in, i, 110  
     in wood naphtha, i, 103  
     estimation of, i, 115  
     in aqueous solution by the freezing-point  
         method, i, 129  
     by the boiling-point method, i, 126; ix, 4  
     in commercial chloroform, i, 278, 279  
     in essences, i, 102, 129  
     in fusel oil, i, 130  
     of methyl alcohol, in the presence of, ix, i  
     in the presence of fixed matters, i, 124  
     small quantities of, in ether, i, 229  
     in tinctures, iv, 102, 129  
     and proof spirit, calculation of the corre-  
         sponding percentages of, i, 123  
     separation of camphor from, iv, 200  
     solidification of, i, 110  
     specific gravity of, i, 110  
     United States Pharmacopœia standards  
         for, i, 112  
     and water, mixtures of, alteration of spe-  
         cific gravity with temperature, i,  
         122  
     estimation of alcohol in, i, 115  
     table of specific gravities of, i, 115  
     in wines, i, 183
- aldehyde**. See *Acetaldehyde*.  
     benzoate, iii, 416  
     blue, v, 251  
     bromide, i, 248  
     butyrate, i, 523  
         formation of, from butter fat, i, 523  
     carbamate, i, 248; vii, 287  
         assay of, i, 249  
         tests for purity of, i, 249  
     chloride, i, 247; ix, 18  
         boiling point of, i, 247  
         detection of, in commercial chloroform, i,  
             277  
         ethyl alcohol in commercial, i, 248  
         specific gravity of, i, 247  
     cinnamate, iii, 439  
     citrate, detection of, in essential oils, ix, 331  
     dithiocarbonates. See *Xanthates*.  
     eosin, v, 297, 304  
     ether, i, 227; ix, 18  
         anhydrous, i, 228  
         boiling point of, i, 227  
         commercial, i, 228  
         detection of alcohol in, i, 229  
             of ethyl nitrite in, i, 231  
             when mixed with chloroform, i, 278  
         estimation of small quantities of alcohol in  
             i, 229  
         impurities in, i, 230

- Ethyl alcohol**, physical properties of, I, 227  
     preparation of, I, 227  
     specific gravity of, I, 227  
   formate, formation of, I, 520  
   green, V, 242, 260, 274, 276  
   hydrazine, VI, 29  
   hydrogen sulphate, preparation of, I, 239  
   morphine, VI, 390; IX, 500  
   nitrite, I, 241  
     detection of, in ether, I, 231  
     spirit of nitrous ether, I, 246  
     determination of, in spirit of nitrous ether,  
       I, 245  
     preparation of, I, 242  
     properties of, I, 242  
   oleate, II, 412  
   orange, V, 458  
   oxide. See *Ethyl ether*.  
   purple, V, 461, 606  
     6 B, V, 276  
   stearate, II, 401  
   sulphates, I, 239  
   sulphuric acid, I, 240  
**Ethylamine**, VI, 11, 20  
   as a putrefaction base, VII, 345  
**Ethylamines**, VI, 19  
**Ethylaniline**, VI, 88, 91  
**Ethyl-benzaconine**, VI, 265  
**Ethylene blue**, V, 354  
   dichloride, detection of, in commercial chloro-  
     form, I, 277  
   and ethylidene chloride, distinction be-  
     tween, I, 248  
   lactic acid, VII, 451  
**Ethylene-diamine**, VII, 196  
**Ethylene-ethenyl-diamine**, VII, 201  
**Ethylidene chloride**, I, 248  
   and chloroform, distinction between, I, 248  
   and ethylene dichloride, distinctions between,  
     I, 248  
**Ethylpyridines**, VI, 144  
 **$\beta$ -Eucaine**, detection of, IX, 495  
**Eucaines**, tests for cocaine in the presence of, VI,  
   334  
**Eucalyptol**. See *Cineol*.  
**Eucalyptus oils**, IV, 244, 249, 250, 336, 442; IX, 359  
   composition of, IV, 336, 341, 343  
   detection of phellandrene in, IV, 339  
   estimation of cineol in, IV, 339; IX, 359  
   varieties of, IV, 343  
**Eucarvone**, IV, 216  
**Eudeamic acid**, IV, 342  
**Eudesmol**, IV, 341, 342; IX, 343  
**Eugallol**, III, 538  
**Eugenol**, IV, 255, 291, 293  
   in clove oil, IV, 330, 331  
   detection of, in oil of cinnamon, III, 444  
   estimation of, IV, 294  
   in essential oils, IV, 242  
   production of vanillin from, III, 515  
**iso-Eugenol**, IV, 294  
**Eugenyl benzoate**, III, 416  
**Euphorin**, VI, 87  
**Euquinine**, IX, 519  
**Eurhodines**, V, 319, 320  
**Eurhodols**, V, 321  
**Eutectic mixtures in fatty acids**, II, 387  
**Euxanthic acid**, VII, 395, 396  
**Ewer's method for estimation of starch in cereals**,  
   IX, 76  
**Excelsin**, VIII, 109  
**Explosive gelatin**, examination of, III, 604  
**Explosives**, III, 559  
   Abel heat test for, III, 595  
     modification of, III, 612  
     precautions in applying, III, 606  
     United States directions for, III, 603  
   composite, III, 591  
   composition of, III, 590  
   detection of nitrocellulose in, III, 562  
     of mercury in, III, 608  
     of metallic mercury in, III, 610  
     of nitroglycerin in, III, 571  
     of picric acid in, III, 578  
   estimation of nitrocellulose in, III, 562  
     of nitroglycerin in, III, 572  
     of picric acid, in, III, 578  
   explosion test for, III, 614  
   fume tests for, III, 612  
   German 135° test for, III, 613  
   Guttmann's test for, III, 612  
   nitroglycerin, moisture in, III, 592  
   propellant, III, 559  
   Spica's test for, III, 612  
   stability tests for, III, 594  
   U. S. Army Ordnance 115° test for, III, 616  
   Vieille test for, III, 612  
   Waltham Abbey silvered vessel test for, III,  
     614  
   Will test for, III, 615

## F

- Fabrics dyed**, estimation of indigo in, V, 402  
   general reactions of dyes for, V, 539  
**Fahrenheit and Centigrade degrees**, table of  
   comparison of, III, 619  
**Fahrlon's method for the examination of oxidised  
   oils**, II, 367  
**Fanto's method for the estimation of glycerol in  
   oils and fats**, II, 477  
**Farnesol**, IX, 342, 343  
**Fast acid blue R**, V, 308  
   green BB extra, V, 576  
   ponceau, V, 156  
   scarlet, V, 156  
   violet B, A 2 R, V, 308  
   10 B, V, 606  
**azo-granat**, V, 174  
**black**, V, 346  
   B, V, 222, 380  
   BS, V, 222  
**blue**, V, 252, 270, 461  
   B, V, 327  
   2 B for cotton, V, 342  
   black, V, 346  
   greenish, V, 327  
   R, V, 327, 330  
   RR, V, 327  
   III, R, V, 341



- Fast acid, bluish-violet, v, 606**  
   brown, v, 163, 166, 610  
     3 B, v, 152, 610  
     (Bayer), v, 166  
     G, v, 163, 166  
     N, v, 148, 159  
     RG, v, 610  
   cotton, blue, B, v, 342  
     R, RR, 3 R, crystals, v, 341  
   green, v, 241, 276, 278, 570  
     bluish, v, 462  
   extra (bluish), v, 276  
     G, v, 348  
     M, v, 346  
     S, v, 274  
   light green, v, 572  
     yellow G, v, 586  
   marine blue, v, 341  
     BM, v, 348  
     G, v, 348  
     GM, v, 342, 348  
     MM, v, 341  
     RM, v, 341, 348  
   myrtle green. See *Dinitroresorcinol*.  
   neutral violet, v, 461  
     B, v, 330  
   new blue for cotton, v, 336  
   ponceau, v, 174  
     B, v, 170, 540  
     2 B, v, 170  
   red, v, 452  
     A, v, 150, 546  
     B, v, 152, 156, 546  
     BT, v, 152, 546  
     C, v, 150, 546  
     D, v, 150, 546  
     E, v, 152, 546  
   scarlet, v, 162, 170  
   violet, v, 604  
     B, v, 172, 546  
     10 B, v, 276  
     R, v, 172, 546  
   wool green (Kalle), v, 276  
   yellow, v, 138, 144, 145, 458  
     extra, v, 138  
     N, v, 138, 466  
     R, v, 138, 141, 144
- Fats, acids, free in, II, 9**  
   alcoholysis of, II, 13  
   analysis of, by saponification, II, 14; IX, 118  
   animal and vegetable, identification of, II, 71, 89  
   artificially coloured, removals of dyestuff from, II, 10  
   bromine substitution value for, II, 27  
     thermal method for the determination of the unsaturation of, II, 60  
   value for, II, 26; IX, 118  
   classification of, II, 64  
     according to their saponification values, II, 17  
   cold, saponification of, II, 16  
   commercial, separation of, by pressure, II, 7  
   constitution of, II, 7; IX, 118  
   critical temperature of, solution of, II, 63
- Fats, detection of, cholesterol in, IX, 118**  
   mineral acids in, II, 75  
   phytosterol in, IX, 118  
   determination of the acetyl value of II, 32; IX, 121  
   acid value of, II, 9  
   the Reichert value for, II, 22  
     with Wollney's modifications, II, 23  
   solidification point by the A. O. A. C. method, II, 56  
   Shukoff's method, II, 57  
   Wolfbauer's method, II, 57  
   specific gravity of, I, 15  
   Hager's method, II, 48  
   distinction between various, by the critical temperature of solution, II, 63  
   Valenta test, II, 62  
   electrical conductivity of, II, 45  
   estimation of, II, 4  
   in butter, II, 307  
   condensed milk, VIII, 213  
   cream, VIII, 187  
   in flour, I, 454  
   glycerol in, II, 477; IX, 222  
   the iodine value of, by Wij's method, II, 31; IX, 120  
   in milk, VIII, 148  
   examination of, for foreign matters, II, 74  
   extraction of, II, 3; IX, 117  
   fatty acids from II, 19, 75; IX, 118  
   heat of combustion of, II, 45  
   Hehner value for, II, 20  
   hydrolysis of, II, 10  
   identification of, II, 84  
     by specific gravity, II, 87  
   iodine values for, II, 29, 392; IX, 118, 120  
   melting points of, II, 51  
     determination by the A. O. A. C. method, II, 54  
       formation of an electric circuit, II, 54  
   properties of, II, 1  
   proportion of acids and glycerol obtained from, II, 12  
   refractive power of, II, 42  
   saponification of, with alcoholic alkali, II, 13; IX, 118  
   softening point of, II, 53  
   solidifying points of, II, 51  
     determination by Dalican's method, II, 55  
     determination by Pinken's method, II, 56  
   solubilities of, II, 61  
   in glacial acetic acid, II, 62  
   specific gravity of, II, 46  
   table of the iodine values of, II, 32  
     Reichert-Meissl values for, II, 26  
     of the true acetyl value of, II, 35  
     values obtained for, with the oleodensitometer, II, 44  
   titer test for, II, 56  
   Valenta test for, II, 62  
   yields of, from different seeds and nuts, II, 4  
   See also *Oils, fixed*.
- Fatty acids, I, 514**  
   acetyl value of, II, 32, 389  
   eutectic mixtures in, II, 387

- Fatty acids, examination of, in fats, IX, 118**  
 higher, II, 371  
 combining weights of, II, 379, 380  
 constants for, II, 379, 380  
 estimation of, by Kottstorfe's method, II, 377  
 by means of Hiebl's solution, II, 378  
 by titration, II, 376  
 from the melting and solidifying points, II, 379  
 without separation, II, 376  
 melting points of, II, 379, 380, 381, 386  
 recognition of, II, 376  
 solidifying points of, II, 379, 380, 381  
 specific gravity of, II, 379  
 iodine values of, II, 391, 392; IX, 120  
 mean molecular weight of, II, 378  
 mixed, estimation of stearic acid in, II, 393  
 separation of, II, 381, IX, 185  
 by the melting point, II, 388, 389  
 and oils, separation of, II, 83, 395  
 properties of, II, 375  
 and resin acids, separation of, II, 77, 395; IV, 30, 33, 73  
 saturated and unsaturated, separation of, II, 392  
 oils, detection of rosin oil in, IV, 44  
 estimation of, in mineral lubricating oil, III, 169  
 and hydrocarbon oils, separation of, II, 18
- Fehling's solution, preparation of, I, 318**  
 modified, for the examination of urine I, 395  
 use of for estimation of sugars gravimetrically, I, 323  
 volumetrically, I, 319
- Fellic acid, VII, 416**
- Fenchene, IV, 168, 183; IX, 325**
- Fenchone, IV, 211**
- Fenchyl alcohol, IV, 279; IX, 343**
- Fennel oil, IV, 442; IX, 360**
- Fenton rubber, IV, 152**
- Fenton's test for carbohydrates, I, 302**
- Fermented milk. See under Milk.**
- Fern-tannin, V, 7**
- Ferric acetate, I, 512**  
 tincture of, I, 512  
 ammonium citrate, I, 567  
 benzoate, III, 415  
 carbonyl ferricyanide, VII, 532  
 citrate, I, 566  
 salicylate, III, 488
- Ferricyanides, VII, 524**  
 detection of, VII, 527  
 estimation of, VII, 528  
 in the presence of cyanides, thiocyanates and ferrocyanides, VII, 552
- Ferrocyanides, VII, 503**  
 carbonyl, IX, 588  
 detection of, VII, 509  
 cyanides in the presence of, VII, 510  
 estimation of, VII, 510; IX, 588  
 in cyanide solutions, VII, 491  
 in the presence of thiocyanates, cyanides and ferricyanides, VII, 552  
 in soda-lyes, VII, 513  
 in spent gas purifying mass, VII, 515
- Ferrous acetate, I, 512**  
 ferricyanide, VII, 526  
 lactate, VII, 446  
 thiocyanate, preparation of and use as an indicator in the Soxhlet's method of estimating sugars, I, 322
- Ferrum tartaratum, I, 553**
- Ferulic acid, III, 448**  
 occurrence of, in resins, IV, 3
- Feverfew oil, IV, 443**
- Fibres, animal, VIII, 632**  
 identification of dyestuffs on, v, 489  
 crude, estimation of, I, 66, 70, 437  
 of cellulose, lignin and cutin in, I, 437  
 detection of alizarin and its allies in, v, 225  
 dyed, chemical examination of, v, 485; IX, 419  
 physical examination, v, 482; IX, 419  
 test of the fastness of dyes in, v, 482; IX, 419  
 estimation of furfural from, I, 437  
 in paper, I, 478  
 red-dyed, examination of, v, 486  
 vegetable, identification of dyestuffs on, v, 516
- Fibrinogen, VIII, 91**
- Fibrinoglobulin, VIII, 91**
- Fibroids, VIII, 631**
- Fibroin, VIII, 635**
- Finkener's method for the determination of the solidification points of fats and oils, II, 56**
- Fir-cone oil, IV, 443**
- Firmitas, VIII, 249**
- Firseed oil. See Pine nut oil.**
- Fish, VIII, 457; IX, 621**  
 analyses of varieties of, VIII, 461  
 cooked, analyses of, VIII, 458  
 cured, VIII, 465  
 flesh, composition of, VIII, 457; IX, 621  
 muscle, partition of nitrogen in, IX, 621  
 oils, II, 221, 223, 226  
 detection of, in olive oil, II, 118  
 in linseed oil, II, 340  
 in rape oil, II, 130  
 in vegetable, oils, IX, 189
- Fish-roe, analysis of, VIII, 460**
- Fixed oils. See Oils, fixed.**
- Flaked barley, composition of, I, 464**
- Flash powders, photographic, III, 617**
- Flavaniline, v, 359, 366, 457**  
 detection of, v, 445  
 S, v, 360, 366
- Flavanthrene R, v, 586**
- Flavazol, v, 580**
- Flaveosine, v, 362, 364, 368**
- Flavin, v, 412, 578**
- Flavindine, v, 387**
- Flavinduline, v, 330**
- Flavophenin, v, 177, 178**
- Flavopurpurin, v, 213, 218, 463**  
 and alizarin, distinction between, v, 215  
 anthropurpurin, distinctions between, v, 214  
 detection of, v, 447
- Flavoring extracts, colouring matters, v, 655**
- Fleabane oil, IV, 443**

- Flesh**, changes in, following death, VIII, 308  
 constituents, separation of, VII, 318  
 isolation of xanthine bases from, VII, 326
- Floridin**, II, 165
- Flour**, I, 454; IX, 593  
 adulteration of, I, 456  
 analysis of, I, 454  
 cold water extract of, I, 455  
 comparison of varieties of, I, 453  
 detection of alum in, I, 457  
   of bleaching agents in, I, 461  
   of copper sulphate in, I, 457  
   of ergot in, I, 458; VII, 23  
   of maize in, I, 462  
   of potato flour in, I, 462  
   of rice flour in, I, 463  
   of sawdust in, I, 462  
 determination of the strength of, VIII, 99  
 doughing test for, I, 454  
 estimation of acidity of, I, 455  
   of ash in, I, 454  
   of diastatic power of, I, 455  
   of ergot in, VII, 23  
   of fat in, I, 454  
   of gliadin in, I, 455; VIII, 101  
   of gluten in, I, 454; VIII, 99  
   of moisture in, I, 454; IX, 593  
   of starch in, I, 454  
 gluten, VIII, 102  
   test for, I, 454  
 Logwood test for alum in, I, 457  
 mineral constituents of, I 456; IX, 593  
 potato, detection of, in wheat flour, I, 462  
 ratio of gliadin to total gluten in varieties of, I, 455  
 separation of plaster of Paris from, I, 458  
 strength of, I, 453  
 wheaten, detection of other flours in, I, 461  
 and oat meal, analysis of a mixture of, I, 418
- Flours**, analyses of, I, 452  
 mixed, I, 461
- Fluavil**, IV, 6, 158
- Fluckiger's test** for aloes, VII, 145, 146
- Fluoran** and its dyestuffs, V, 286
- Fluoranthene**, III, 267, 269  
 behaviour of, with chromic acid, III, 279  
 compound of, with picric acid, III, 275
- Fluorene**, III, 266, 269  
 behaviour of, with chromic acid, III, 278  
 compound of, with picric acid, III, 275
- Fluorescein**, III, 338, 546, 547; V, 290, 457, 546  
 constitution of, V, 287, 292  
 production of, from glyceryl phthalate, III, 544  
 substitution derivatives of, V, 293  
 uranin, V, 304
- Fluorescence**, I, 40
- Fluorescent blue**, V, 343, 346, 467  
 resorcin blue, V, 343
- Fluorescin**, V, 291
- Fluorides**, detection of, in butter, II, 312; VIII, 690  
 in cream, VIII, 190, 690  
 estimation of, in wines, I, 176
- Fluormethæmoglobin**, VIII, 543
- Foam test** for butter, II, 299
- Fodders**, value of, VIII, 93
- Foenugreek oil**, IV, 443
- Food**, detection of coal-tar colours in, V, 642  
 of impurities in, I, 75  
 of salicylic acid in, III, 477  
 formic acid and sodium formate as preservatives in, I, 521  
 poisonous, VII, 343
- Foods**, canned, estimation of metals in, VIII, 340  
 colouring matters in, V, 623; IX, 449  
 containing tannin, estimation of salicylic acid in, III, 485  
 detection of benzoic acid in, III, 405, 410  
   of cochineal in, V, 423  
   of colouring matters in, V, 645, 666; IX, 449  
   of  $\beta$ -naphthol in, III, 257  
   of saccharin in, III, 431  
 estimation of benzoic acid in, III, 412  
   of methyl salicylate in, III, 493  
   of saccharin in, III, 433  
   of salicylic acid in, III, 484  
 flesh, detection of colouring matters in, V, 649  
 infants', VIII, 232  
 preservatives in, regulations for, IX, 597
- Force**, composition of, I, 464
- Formaldehyde** and acetaldehyde, separation of, I, 264  
 Bonnet's test for, I, 258  
 detection of, in cream, VIII, 192  
   in milk, I, 259; VIII, 171  
 dimethylaniline test for, I, 259  
 estimation of, I, 260  
   methyl alcohol in, I, 93  
   in milk, VIII, 172  
 formation of, I, 256  
 fuchsin test for, I, 257  
 hydrochloric acid test for, I, 258  
 iodometric method for the estimation of, I, 261  
 $\beta$ -naphthol test for, I, 257  
 oxidation of, I, 256  
 phenol test for, I, 259  
 phenylhydrazine-nitroprusside test for, I, 258  
   influence of vanillin on, I, 260  
 phloroglucinol test for, I, 258  
 physical properties of, I, 256  
 resorcinol test for, I, 259  
   influence of vanillin on, I, 260  
 salicylic acid test for, I, 258  
 Shrewsbury-Knapp test for, I, 259  
 solutions, assay of, I, 569  
 sulphuric acid test, influence of vanillin on, I, 260  
 tests for, I, 257  
 use of, as a food preservative, I, 257
- Formalin**, I, 257  
 action of, on casein, VIII, 125
- Formanilide**, VI, 86
- Formates**, I, 520  
 See also *Parent substance*.
- Formic acid**, I, 519  
 and acetic acids, action of, on mercuric chloride, I, 520  
 separation of, I, 521  
 action of oxidizing agents on, I, 520

**Formic acid**, colour reactions of, I, 487  
     detection of, in cream, VIII, 191  
     as a preservative in food, I, 521  
     by reduction to formaldehyde, I, 521  
     estimation of, I, 521  
     in acetic acid, I, 494  
     by the reduction of mercuric formate, I, 520  
     production of, from oxalic acid, I, 528  
     tests for, IX, 97  
     aldehyde. See *Formaldehyde*.  
**Formogelatin**, VIII, 600  
**Formolite**, IX, 235, 238  
**Formyl blue B**, v, 600  
     violet, v, 462  
     4 B S, v, 606  
     S 4 B, v, 258, 276  
**Formyl-*p*-naphthalide**, VI, 113  
**Formyl-*p*-phenetidin**, VI, 104  
**Foster automatic oil-tester**, III, 125  
**Frankincense oil**, IV, 443  
**French turpentine**, IV, 76, 80  
**Freund's acid**, VI, 122  
**Fröhde's reagent for alkaloids**, VI, 200  
 **$\alpha$ -Fructose**. See *Lævulose*.  
**Fruit**, canned, tin in, VIII, 338  
     colouring matters from, v, 633  
     juices, estimation of benzoic acid in, IX, 284  
         of citric acid in, I, 562; IX, 113  
         of malic acid in, IX, 98  
         of tartaric acid in, IX, 106  
     products, detection of artificial colouring in, VIII, 383  
     sugar. See *Lævulose*.  
     syrops, colouring matters in, v, 655  
     and flowers, candied, colouring matters in, v, 658  
**Fuchsia**, v, 334, 454  
**Fuchsin test for formaldehyde**, I, 257  
**Fuchsine**, v, 278, 472  
     detection of, v, 449  
     new, v, 278  
     S, v, 268  
**Full-cream lactogen**, VIII, 218  
**Fuller's earth test for petroleum**, III, 48  
**Fulminate of mercury**. See *Mercuric fulminate*.  
**Fulminic acid**, VII, 541  
**Fulminuric acid**, VII, 542  
**Fungus spores in commercial cane sugar**, I, 354  
**Furfural**, I, 255  
     estimation of, with phloroglucinol, I, 402  
     in potable spirits, I, 196  
**Furfuraldehyde test for sesame oil**, II, 143  
**Furze**, alkaloid of, VII, 13  
**Fusel oil**, determination of, in spirits, I, 518  
     estimation of ethyl alcohol in, I, 130  
**Fusible calculus**, VII, 388  
**Fustet wood**, v, 408  
**Fustic**, v, 409, 634  
     commercial preparations of, v, 410  
     extract, v, 637  
     old, v, 408, 578  
     young, v, 408, 578, 634  
**Fustin, patent**, v, 463, 580  
**Fustine**, v, 410

## G

**Gadolinic acid in cod-liver oil**, II, 214  
**Gadus histone**, VIII, 91  
***d*-Galactan**. See *Gelose*.  
**Galactose**, I, 376  
     and dextrose, separation of, I, 376  
     estimation of, I, 377  
     formation of mucic acid from, I, 376  
     mutarotation of, I, 376  
     specific rotation of, I, 376  
**Galactose- $\alpha$ -methylphenylhydrazone**, I, 376  
**Galafer milk**, VIII, 216  
**Galam butter**. See *Shea butter*.  
**Galangal oil**, IV, 443  
**Galanilide**, III, 535  
**Galbanoresinotannol**, IV, 4  
**Galbanum**, IV, 97; IX, 318  
     oil, IV, 443  
**Galician petroleum**, III, 43, 50  
**Gallacetophenone**, III, 428, 535  
**Gallamine blue**, v, 345, 348, 462, 592  
**Gallanilic blue P**, v, 463  
     green, v, 348  
     indigo, v, 348  
     PS, v, 462  
     violet BS, v, 348, 462  
**Gallanilid**, VI, 86  
**Gallanol**, III, 535  
**Gallazine A**, v, 348  
**Gallein**, III, 547, 557; v, 298, 304, 449, 462, 604  
     detection of, v, 447  
     salts of, v, 298  
**Gallic acid**, III, 525  
     conversion of, into benzoic acid, III, 527  
     derivatives of, and their use in medicine, III, 533  
     detection of, in commercial gallotannic acid, v, 22  
     effect of heat on, III, 526  
     estimation of, III, 529, 531  
     gallotannic acid and pyrogallol, distinctions between, III, 530  
     preparation of, III, 525  
     reactions of, III, 528; v, 51  
     solubility of, III, 526  
**Gallicin**, III, 534  
**Gallisin**, I, 379  
**Gall-nuts**, analysis of, v, 35  
     Chinese and Japanese, v, 36  
**Gallobromol**, III, 535  
**Gallocyanine**, v, 344, 348, 462, 463, 604  
     detection of, v, 447, 454  
     of logwood in the presence of, v, 408  
**Galloflavin**, v, 218, 463, 527, 578  
     detection of, v, 447  
**Gallotannic acid**, v, 7, 16, 43  
     analysis of, v, 22  
     commercial v, 21  
     detection of gallic acid in, v, 22  
     of impurities in, v, 21  
     estimation of the pure acid in, v, 22  
     constitution of, v, 17; IX, 385  
     detection of, in brandy, I, 199  
     estimation of, IX, 404

- Gallotannic acid, extraction of, from gall-nuts  
by method of Pelouze, v, 2  
gallic acid and pyrogallol, distinctions  
between, III, 530  
preparation of, v, 2; IX, 385  
properties of, v, 19  
and quercitannic acid, distinctions between,  
v, 25  
reactions of, v, 7, 20, 51  
as a reagent for alkaloids, VI, 187  
reduction equivalent of, v, 64  
synthesis of, v, 16  
in tea. See *Tannin in tea*.  
in yeast, I, 209
- Galls, v, 35  
analysis of, v, 67
- Gall-stones, VII, 410
- Gambenè extract, reactions of, v, 45
- Gambier, v, 412  
analysis of, v, 102  
catechins from, v, 28, 30  
and catechu, distinction between, v, 34  
decomposition products of, v, 55  
reactions of, v, 43, 46
- Gambin, v, 570, 612  
B, v, 130  
R, v, 130, 131, 463  
Y, v, 130, 131, 463
- Gamboge, v, 408, 416
- Gambogic acid, v, 416
- Game, composition of, VIII, 270
- Gardenia oil, IV, 443
- Garlic oil, IV, 443
- Garnet B, oxochrome, v, 552  
lac, IV, 67  
shades, examination of, v, 510
- Garouille, reactions of, v, 45
- Gas liquor, estimation of thiocyanates, VII, 554  
oil, III, 136  
apparatus for the determination of the gas  
value of, III, 139  
candle power of gas obtained from, II, 140  
products yielded by varieties of, III, 136,  
137
- Gasolene, III, 111
- Gasometric method for the estimation of formal-  
dehyde, I, 262
- Gastric juice, IX, 580
- Gas-works tar, analyses, typical, III, 26  
assay of, III, 25  
constituents of, III, 22, 24  
determination of water in, III, 28  
distillation of, III, 20, 23  
fractional distillation of, III, 21
- Gaultheria, methoxyl number, IV, 242  
natural, III, 493; IX, 305
- Gedanite, IV, 18
- Geddah gum, acid from, I, 439
- Gelatin, VIII, 91, 587, 614  
bacterial decomposition of, VIII, 598  
blasting, application of the Abel test to, III,  
602  
test for mercury in, III, 609  
cleavage products of, VIII, 594  
in commercial honey, I, 385
- Gelatin, detection of, IX, 605  
in cream, VIII, 193  
in formogelatin, VIII, 601  
in milk, VIII, 166  
dynamite, application of Abel test to, III, 602  
estimation of, in meat extracts, VIII, 414  
in paper, I, 477  
food, VIII, 616  
estimation of sulphurous acid and sulphites  
in, VIII, 617  
and glue, distinctions between, VIII, 601  
reactions of, VIII, 589  
substitutes, VIII, 621  
suitability of, for photographic purposes, VIII,  
614  
tannate of, VIII, 590  
technical, VIII, 614  
ultramicroscopic structure of, IX, 604  
use of, in tannin analysis, IX, 606
- Gelatones, VIII, 595, 597
- Gelatoses, VIII, 594
- Gelose, I, 437, VIII, 622  
estimation of, I, 377
- Gelsemic acid, VII, 34
- Gelsemine, VII, 30  
extraction of, VII, 31  
and gelseminine, separation of, VII, 34
- Gelseminine, VII, 30, 33
- Gelsemium, alkaloids of, VII, 30
- Genisteine, IX, 483  
salts of, IX, 483
- Gentian blue 6 B, v, 251, 284
- Gentianine, v, 356
- Geranin, v, 546
- Geraniol, IV, 254, 258, 263, 267  
and citronellol, separation of, IV, 259, 264  
in otto of rose, IX, 329  
commercial, IV, 261  
constitution of, IV, 258; IX, 341  
detection of, IV, 260  
in rose oil, IV, 383  
estimation of, in citronella oil, IX, 328  
group, IV, 258
- Geranium oil, IV, 244, 343, 443; IX, 361  
Indian, IV, 309, 444
- Gerhardt's reaction for aceto-acetic acid, VII, 401
- Gerland's process for the estimation of tannin, v, 89
- German 135° test for explosives, III, 613
- Gerontine, VII, 352
- Ghedda wax, II, 268
- Ghee, IX, 175
- Gin, I, 203
- Ginger, detection of, in vinegar, I, 504  
oil, IV, 444; IX, 362
- Ginger-grass oil, IV, 304, 309; IX, 347
- Gingili oil. See *Sesame oil*.
- Girofle, v, 454
- Gitalin and digitoxin, separation of, IX, 547
- Gitogen, IX, 547
- Gitonin, IX, 547
- Glacier blue, v, 276
- Glessite, IV, 18
- Gliadin, VIII, 97  
estimation of, in flour, I, 455; VIII, 101  
preparation of, I, 455

- Globulin of oil seeds**, VIII, 109  
wheat, VIII, 97
- Globulins**, VIII, 33, 91  
and albumins, difference, between, VIII, 33  
extraction of, VIII, 61  
plant, preparation of, VIII, 68  
vegetable, VIII, 94
- Gloy**, I, 429
- Gluconasturtium**, VII, 106
- d-Glucose**. See *Dextrose*.
- Glucose commercial**. See *Starch-sugar*.
- Glucose-vinegar**, I, 498
- Glucoses**, I, 287, 372
- Glucosides**, I, 391; VII, 95; IX, 545  
action of enzymes on, I, 391  
classification, VII, 96  
cyanogenetic, I, 391; VII, 101; IX, 545  
analysis of, I, 392  
determination of the hydrocyanic acid  
obtainable from, I, 392  
detection of, I, 391  
differentiation between  $\alpha$  and  $\beta$  dextroses in,  
I, 392  
extraction of, I, 391  
identification of sugar present in, I, 392  
of conifers, VII, 99  
of digitalis, VII, 116  
of jalap, VII, 130  
of mustard, VII, 103  
of poplar, VII, 99  
of scammony, VII, 130  
of strophanthus, VII, 121  
synthetic, IX, 545  
table of, VII, 97  
of willow, VII, 99
- Glucoliopaeolin**, VII, 106
- Glucuronic acid**, I, 399  
detection of in the presence of pentoses, I, 400  
and glucose, distinction between, I, 399  
estimation of, I, 399
- Glue**, VIII, 601  
ash of, VIII, 610  
Cadet's test for, VIII, 611  
chemical tests for, VIII, 611  
detection of, in sizing materials, IX, 605  
estimation of acid in, VIII, 611  
non-gelatinous substances in, VIII, 612  
water in, VIII, 610  
finger test for, VIII, 606  
jelly strength of, VIII, 606  
keeping properties of, VIII, 609  
liquid, VIII, 621  
manufacture of, VIII, 602  
melting point of, VIII, 610  
Schattenmann's test for, VIII, 611  
selection of, for various purposes, VIII, 614  
standards, for, VIII, 608  
strength of, VIII, 613  
tests for, VIII, 605  
viscosity of, VIII, 605
- Glusidum**. See *Saccharin*.
- Glutamic acid**, VII, 243  
estimation of, in protein hydrolysis, IX, 592  
separation of from the hydrolysis products of  
proteins, VIII, 27
- Glutamine**, VII, 242  
isolation of, from vegetable juices, VII, 239
- Glutelin of maize**, VIII, 107
- Glutelins**, extraction of, VIII, 61  
vegetable, VIII, 94
- Gluten**, VIII, 99  
composition of, I, 455  
estimation of, in flour, I, 454  
flour and bread, VIII, 103  
test for flour, I, 454
- Gluten-glue**, VIII, 621
- Glutenin**, I, 455; VIII, 97
- Glutenins**, VIII, 34
- Glucose**, IX, 50
- Glycerides**, II, 8  
alcoholysis of, II, 13  
mixed, presence of, in fats, II, 8
- Glycerinum**, IX, 220
- Glycerol**, II, 447; IX, 211  
action of, on borax, II, 454  
ferric chloride on, II, 452  
mercuric chloride on, II, 452  
analysis of, II, 467; IX, 211  
boiling point of, II, 447; IX, 211  
commercial II, 466  
crude, II, 466  
and distilled, distinction between, II, 476  
detection of, II, 453  
in coffee berries, VI, 652  
distillation, II, 467  
distilled, II, 471  
and crude, distinction between, II, 476  
dynamite, II, 471  
detection of arsenic, in, II, 472  
esters of, II, 452; III, 575  
estimation of, II, 455, 477; IX, 214  
by the acetin method, II, 460; IX, 214  
by oxidation with permanganate, II, 457,  
465  
potassium dichromate, II, 459, 465; IX,  
217  
by physical methods, II, 463  
by Shukoff and Schestapoff's method, II,  
463  
comparison of methods, II, 465  
gravimetrically, II, 461  
in oils and fats, II, 477  
in soap, II, 434  
in soap-lyes, II, 478  
from the specific gravity, II, 463  
volumetrically, II, 457  
in wines, I, 166; IX, 221  
by Zeisel and Fanto's method, II, 461,  
466, 477; IX, 222  
evaporation of, II, 456  
formation of acrolein from, II, 453  
glycerylphosphoric acid from, II, 452  
nitroglycerin from, II, 452  
impurities in, IX, 221  
international standard methods of analysis  
of, IX, 211  
isolation of, after saponification, II, 21  
melting point of, II, 447  
nitrates of polymerised, III, 575  
oxidation of, II, 451

- Hæmatoporphyrin**, VIII, 552  
 detection of, in urine, VIII, 555  
 oxidation products of, VIII, 557  
 spectrum of, VIII, 554
- Hæmatoxylin**, v, 403  
 use of, in the estimation of alkaloids, vi, 183
- Hæmin**, VIII, 546  
 oxidation products of, VIII, 557  
 test for blood stains, VIII, 574
- Hæmochromogen**, VIII, 549
- Hæmocyanin**, VIII, 559
- Hæmoglobin**, VIII, 91, 504, 506, 526  
 aloin test for, VIII, 524  
 benzidine test for, VIII, 524  
 carbon-monoxide. See *Carboxyhæmoglobin*.  
 chemical properties of, VIII, 522  
 derivatives of, VIII, 529  
 estimation, VIII, 559  
 formation of, from oxyhæmoglobin, VIII, 527  
 guiacum test for, VIII, 522, 526  
 hydrolysis of, VIII, 544  
 malachite green test for, VIII, 524  
 nitric oxide, VIII, 536  
 and oxygen, heat of combination of, VIII, 522  
 paraphenylenediamine hydrochloride test for, VIII, 525  
 phenolphthalein test for, VIII, 525  
 preparation of, VIII, 508  
 solubility of, VIII, 511  
 spectrum, of, VIII, 512, 529  
 tests for, VIII, 522
- Hæmoglobinometer**, VIII, 562, 564
- Hæmoglobins**, VIII, 35
- Hæmolysis**, VIII, 503
- Hæmometers**, VIII, 563
- Hæmopyrrole**, VIII, 558
- Hager's reagent for alkaloids**, vi, 185  
 test for glycerin, ix, 220
- Hair**, VIII, 676  
 dyes, VIII, 679
- Hake-liver oil**, II, 221
- Halogens**, detection of, in organic substances, I, 62  
 in colouring matters, v, 473  
 estimation of, in organic substances, I, 63
- Halphen's test for cottonseed oil and stearin**, II, 135, 300; IX, 154  
 for the detection of palm oil in butter, II, 310  
 modification of, for colophony, iv, 29
- Hammarstein's test for bile pigments**, VII, 425
- Hams**, VIII, 356  
 composition of, VIII, 365
- Hanoverian petroleum**, III, 44
- Harmaline**, VII, 36
- Harmine**, VII, 35
- Hayduck's method for the determination of the fermenting power of yeast**, I, 223
- Hazelnut oil**, II, 69, 105  
 fatty acids from, II, 105  
 iodine value of, II, 106
- Heat of combustion of oils and fats**, II, 45
- Hedge mustard oil**. See *Mustard oil, hedge*.
- Hedeoma oils**, iv, 445
- Hedychium oil**, iv, 445
- Heerabolene**, IX, 325
- Hehner value for fats and oils**, II, 20
- Hehner's method for the analysis of complex candle mixtures**, II, 262  
 for the estimation of glycerol, II, 459, 465
- Helianthin**, v, 137, 138, 141, 144
- Helichrysum oil**, iv, 445
- Helicin**, VII, 101
- Heligoland blue B**, v, 592  
 yellow, v, 174
- Helindone brown G**, v, 538  
 fast scarlet R, v, 536  
 orange R, v, 535  
 red B, 3B, v, 536  
 scarlet S, v, 536  
 yellow 3G, v, 535
- Heliotrope**, v, 184, 604  
 B, v, 330  
 2B, v, 186, 330, 606  
 ciba, v, 537, 608  
 O, thiogene, v, 610  
 tannin, v, 330
- Heliotropin**, III, 523
- Helleborein**, VII, 81
- Helleborin**, VII, 81
- Hellebores**, alkaloids of, VII, 78  
 estimation of, VII, 83  
 extraction of, VII, 81  
 table showing the properties of, VII, 82
- Heller's test for proteins**, VIII, 36
- Helvetia blue**, v, 280  
 green, v, 242, 276, 453, 570
- Hemicollin**, VIII, 595
- Hemiterpenes**. See *Pentines*.
- Hemlock**, alkaloids in, vi, 212  
 assay of, vi, 221  
 bark, v, 46  
 Canadian, analysis of, v, 67, 102  
 extract, analysis of, v, 67  
 reactions of, v, 43  
 Hoppenstedt test for, ix, 403  
 poisoning by, vi, 216
- Hemlock-tannin**, v, 7
- Hemp fibres**, microscopic appearance of, in paper, I, 475  
 oil, iv, 445
- Hempseed oil**, II, 70, 150; IX, 139
- Henbane**. See *Hyocymus*.
- Henocque's hæmoglobinometer**, VIII, 565
- Henriques' method for the estimation of amino-acids**, VII, 408
- Heptacoline**, vi, 155
- Heptine**, iv, 38
- Herabol myrrh**, iv, 98
- Heracleum oil**, iv, 445
- Herepathite**, vi, 512
- Hermophenyl**, III, 397
- Heroin**, vi, 365, 368, 389; IX, 499
- Herring oil**, II, 226  
 effect of blowing on, II, 367
- Hessian blue**, v, 251, 284  
 brown BB, v, 180  
 2B, v, 612  
 MM, v, 194  
 purple B, v, 198, 542  
 D, v, 198  
 N, v, 198, 542



- Hessian violet**, v, 198, 604  
     yellow, v, 198, 578
- Heteroxanthine**, vii, 322, 331
- Hexacoline**, vi, 155
- Hexamethylene-tetramine**, i, 263  
     analysis of, i, 263  
     detection of, in medicines, i, 263  
     use of, i, 263
- Hexamethyl-triaminophenylacridine**, v, 370
- Hexylamine as a putrefaction product**, vii, 352
- Hide powder**, chroming of, v, 82  
     determination of the acidity in, v, 81  
     official method of chroming, v, 81  
     standardising of, v, 79  
     substitute for, v, 86, 95
- Hilger's method for the determination of mineral acids in commercial vinegar**, i, 505
- Hill calcium chloride tube**, use of, i, 57
- Hinkel test for methyl alcohol**, i, 90
- Hink's test for the detection of coconut and palm-kernel oils in butter**, ii, 301
- Hinsberg's method for the separation of amines**, vi, 4
- Hippuric acid**, vii, 391  
     detection of, ix, 570  
     in commercial benzoic acid, iii, 406  
     in urinary deposits, vii, 383  
     estimation of, vii, 394; ix, 569  
     preparation of, vii, 393  
     properties of, vii, 393  
     reactions of, vii, 393
- Histidine**, vii, 259  
     and arginine, separation of, viii, 29  
     estimation of, by Van Slyke's method, viii, 82  
     separation of, from the products of protein hydrolysis, viii, 29
- Histone**, viii, 92
- Histones**, viii, 33
- Höchst new blue**, v, 276
- Hoenig's process for the estimation of indigotin**, v, 392
- Hofmann violet**, v, 278, 454, 461, 606
- Hoffmann's method for the detection of amines**, v, 445  
     separation of, vi, 5
- Hoi-liver oil**, ii, 221
- Holde's test for mineral oils in sperm oil**, ii, 238
- Holocaine**, detection of, ix, 495
- Homarecoline**, vi, 210
- Homatropine**, vi, 302
- Homocatechol**, iii, 337, 342  
     methyl ether. See *Cresol*.
- Homocinchonidine**, vi, 499, 540
- Homococaine**, vi, 339
- Homogenised milk**. See under *Milk*.
- Homogentisic acid**, vii, 405; ix, 569
- Homolka's base**, v, 235
- Homolle's amorphous digitalin**, vii, 119
- Homo-olestranol**, ii, 488
- Homophosphine G**, v, 584
- $\alpha$ -Homoprotocatechuic acid**, iii, 513
- Homoquinine**, vi, 549
- Homosalicylic acids**. See *Cresotic acids*.
- Honey**, i, 383  
     adulterated with cane sugar and glucose syrup, estimation of, i, 304  
     American, composition of, i, 383  
     artificial, i, 386  
     Canadian, composition of, i, 384  
     commercial, adulterants in, i, 384  
     analysis of, i, 384  
     ash from, i, 384  
     detection of cane sugar in, i, 386  
     dextrin in, i, 385  
     gelatin in, i, 385  
     invert sugar in, i, 385  
     saccharine adulterants in, i, 385  
     starch in, i, 384  
     starch-sugar in, i, 387  
     estimation of cane sugar in, i, 387  
     of insoluble matter in, i, 384  
     of starch-sugar in, i, 387  
     and pure honey differentiation between, i, 388  
     specific rotatory power of, i, 385  
     composition of, i, 383  
     coniferous, dextrin-like substance in, i, 388  
     crystallisation of, i, 383  
     estimation of moisture in, i, 344  
     European, composition of, i, 383  
     separation of beeswax from ii, 242  
     specific, rotatory power of, i, 385
- Honeydew honeys**, i, 383
- Hop oil**, iv, 445; ix, 362
- $\beta$ -Hop-bitter acid**. See *Lupulinic acid*.
- Hoppe-Seyler's test for purine bases**, vii, 331
- Hops**, vii, 164; ix, 550  
     analysis of, commercially, vii, 175; ix, 551, 554  
     antiseptic power, estimation of, vii, 179; ix, 552, 557  
     bitter substances in, vii, 164  
     constituents of, vii, 164; ix, 550  
     detection of sulphuring in, vii, 182  
     estimation, of arsenic in, i, 148; ix, 184, 559  
     of bitterness of, ix, 558  
     of moisture in, vii, 181  
     of resins in, vii, 175; ix, 554, 558  
     of soft resins in by Lintners method, vii, 177; ix, 556  
     of sulphur in, vii, 184  
     of tannin in, v, 91; vii, 187  
     lupulin in, vii, 172  
     morphology of, vii, 170  
     nitrogenous constituents of, ix, 550  
     physical examination of, vii, 189  
     and quassia, method for distinguishing between, in beer, i, 161  
     resins in, vii, 164  
      $\alpha$ - and  $\beta$ - resins in, estimation of, vii, 177  
      $\gamma$ -resin from, vii, 167  
     valuation of, vii, 174
- Hop-substitutes in beer**, detection of, vii, 191
- Hop-tannin**. See *Lupulotannic acid*.
- Hordein**, viii, 103
- Hordenine**, vii, 36  
     formation of, in barley, ix, 477

- Horse fat, II, 72, 206  
 detection of, in tallow, II, 212  
 flesh, VIII, 376  
 glycogen in, VIII, 282, 378  
 testing for, VIII, 273
- Horse mint oil, IV, 445
- Häbl's method for the determination of iodine values, II, 29, 378
- Häfner, spectrophotometer of, VIII, 520
- Humanised milk. See under *Milk*.
- Humulene, IV, 187; VII, 174; IX, 325, 363
- Humulone, VII, 167
- Huppert's test for bile pigments, VII, 426
- Hyalins, VIII, 629
- Hyalogens, VIII, 629
- Hydracetic acid, VI, 32
- Hydracrylic acid, VII, 451
- Hydrargyraseptol, III, 403
- Hydrastine, VI, 564  
 constitution of, VI, 565  
 detection of, VI, 566; IX, 522  
 estimation of, gravimetrically, VI, 570; IX, 522  
 volumetrically, VI, 568  
 reactions of, VI, 566, IX, 522  
 specific rotation of, IX, 478  
 salts of, VI, 571
- Hydrastinine, VI, 572; IX, 522, 524  
 hydrochloride, VI, 573  
 sulphate, VI, 574
- Hydrastis, fluid extract of, assay of, IX, 523  
 Rhizome, assay of, IX, 523
- Hydrazine, VI, 23  
 chlorides, VI, 25  
 detection of, VI, 25  
 estimation of, VI, 26  
 in presence of nitrous acid, IX, 470  
 hydrate, preparation of, VI, 24  
 nitrate, IX, 469  
 salts of, VI, 25  
 sulphate, VI, 24, 25
- Hydrazines, substituted, VI, 28
- Hydrazones, VI, 34
- Hydroacridine, VI, 164
- Hydrobromic ether. See *Ethyl bromide*.
- Hydrocarbons, III, 1; IX, 229  
 aromatic, IX, 234  
 action of formaldehyde on, IX, 235  
 estimation of, in admixture with paraffins, IX, 263  
 unsaturated hydrocarbons in, IX, 264  
 nitration of, IX, 235  
 bromine absorption of, III, 6  
 cyclic, III, 1; IX, 259  
 from coal-tar, III, 197  
 detection of, in beeswax, II, 258  
 of essential oils, IV, 163  
 iodine absorption of, III, 7  
 products yielded by the distillation of various, III, 138  
 separation of by chemical methods, IX, 232  
 by fractional distillation, IX, 229  
 by physical methods, IX, 229  
 solid, behaviour of, with benzal chloride, III, 280
- Hydrocarbons, solid, with chromic acid, III, 278  
 with metallic chlorides, III, 277  
 with solvents, III, 274  
 compounds of, with picric acid, III, 274  
 reactions of, III, 274  
 unsaturated, estimation of, in aromatic hydrocarbons, IX, 264
- Hydrocarbonyl-ferrocyanic acid, VII, 532
- Hydrocarotol, II, 485
- Hydrocelluloses, cupric reducing power of, I, 433
- Hydrochloric acid, detection of, in commercial chloroform, I, 276  
 in gastric juices, IX, 580  
 method for the estimation of starch, I, 420  
 test for formaldehyde, I, 258  
 ether. See *Ethyl chloride*.
- Hydrocinchonidine, VI, 499, 540
- Hydrocinchonine, VI, 499, 542
- Hydrocotarnine, VI, 354, 367, 397
- 1-2 Hydrocoumaric acid, III, 448
- Hydrocoumarin, III, 448
- Hydrocyanic acid, antidotes for, VII, 467, 470  
 detection of, VII, 479; IX, 585  
 in the body, VII, 467  
 in essential oil of bitter almonds, III, 424  
 in the presence of a ferrocyanide or thiocyanate, VII, 479  
 of potassium ferrocyanide, VII, 468  
 minute traces of, VII, 469  
 estimation of, VII, 480, IX, 586  
 in bitter-almond and cherry-laurel water, VII, 466  
 in essential oils, IV, 225; IX, 325  
 in presence of benzaldehyde, IX, 287  
 in vegetable and animal tissues, VII, 470  
 formation of, VII, 462  
 from cyanogenetic glucosides, VII, 101  
 picrate reaction for, VII, 470  
 preparation of, VII, 464  
 properties of, VII, 465  
 toxicology of, VII, 466
- Hydro-ergotinine. See *ergot-oxine*, VII, 18
- Hydroferricyanic acid, estimation of, in presence of ferric salts and cyanides, IX, 588
- Hydroferrocyanic acid, VII, 503
- Hydrogen, estimation of, I, 57; IX, 237  
 cyanate. See *Cyanic acid*.  
 cyanide. See *Hydrocyanic acid*.  
 peroxide, detection of in cream, VIII, 191  
 in milk, VIII, 173  
 effect of, on milk, VIII, 690  
 method for the estimation of formaldehyde, I, 261  
 phosphide, estimation of in commercial acetylene, III, 9, 10  
 sulphide, estimation of in commercial acetylene, III, 9
- Hydro-ipecamine, IX, 542
- Hydrolutidine, VII, 353
- Hydrolysis of esters, I, 232  
 of sugars, I, 296
- Hydrometer, Baumé's, I, 8  
 Beck's, I, 15  
 Cartier's, I, 15  
 Twaddell's, I, 7

**Hydrometers**, I, 7  
**Hydrophthalic acids**, III, 543  
**Hydroquinidine**, VI, 534  
**Hydroquinidine**, VI, 500  
**Hydroquinine**, VI, 500, 533  
     salts of, VI, 534  
     sulphate, VI, 534; IX, 519  
**Hydroquinone**. See *Quinol*.  
**Hydroxyacids**, aromatic, in urine, VII, 404  
**Hydroxyanthraquinones**, formation of, III, 545  
**Hydroxy-azo** colouring matters. See *under Colouring matters*.  
**Hydroxy-benzaldehydes**, III, 499  
**Hydroxybenzene**. See *Phenol*.  
***o*-Hydroxybenzoic acid**. See *Salicylic acid*.  
***p*-Hydroxybenzoic acid**, separation of from salicylic acid, III, 471  
**Hydroxybenzoic acids**, isomeric, III, 465  
 **$\beta$ -Hydroxybutyric acid**, VII, 400; IX, 578  
     estimation of in urine, VII, 403  
**Hydroxycaffeine**, VI, 595  
**Hydroxyfurfuraldehyde**, formation of from carbohydrates, IX, 64  
**Hydroxyketones**, v, 206  
**Hydroxymandelic acid**, VII, 406  
**Hydroxymethylanthraquinone drugs**, detection of, in admixture with aloes, IX, 550  
**Hydroxymethyl-benzoic acids**, III, 506  
**Hydroxy-naphthoic acid**, III, 467  
***p*-Hydroxyphenyl-acetic acid**, detection of in urine, VII, 404.  
**Hydroxyphenyl-acetic acids**, III, 508  
**Hydroxyphenyl -  $\alpha$  - aminopropionic acid**. See *Tyrosine*.  
***p*-Hydroxyphenylethylamine**, as a putrefaction product, VII, 346  
***p*-Hydroxyphenyl-propionic acid**, detection of in urine, VII, 404  
**Hydroxy-iso-phthalic acid**, detection of in salicylic acid, III, 467  
 **$\alpha$ -Hydroxypropionic acid**. See *Lactic acid*.  
 **$\beta$ -Hydroxypropionic acid**, VIII, 451  
**2-Hydroxyquinoline**, VI, 156  
**8-Hydroxyquinoline**, VI, 156  
**Hydroxyquinoline sulphonic acids**, III, 403  
**Hydroxysparteine**, VI, 234  
**Hydroxy-toluic acids**, III, 508, 510  
**Hygrine**, VI, 343  
**Hyochoic acid**, VII, 416  
**Hyo-glycochoic acid**, VII, 414  
**Hyoscine**, VI, 291, 299  
     constitution of, IX, 490  
     hyoscyamine and atropine, distinction between, VI, 303  
     reactions of, VI, 303  
     salts of, VI, 300  
     specific rotation of, IX, 478  
***d*-Hyoscyamine**, VI, 298  
***dl*-Hyoscyamine**. See *Atropine*.  
***l*-Hyoscyamine**, VI, 291, 297  
**Hyoscyamine**, amorphous, VI, 300  
     hyoscine and atropine, distinction between, VI, 303  
     reactions of, VI, 303  
     salts of, VI, 298

**Hyoscyamine**, test for, VI, 307; IX, 491  
**pseudo-Hyoscyamine**. See *Norhyoscyamine*.  
**Hyoscyamus**, alkaloids in, VI, 316  
**Hypnal**, VI, 45  
**Hypnone**, III, 428  
**Hypochlorous acid**, detection of in commercial chloroform, I, 276  
**Hypodermic tablets**, estimation of strychnine in, VI, 462  
**Hypoxanthine**, VII, 321, 334; VIII, 288  
**Hyssop oil**, IV, 345, 445

## I

**Ice colours**, v, 202  
**Ichthulin**, VIII, 92  
**Illuric**, IV, 5  
**Imido-diphenyl**. See *Carbasol*.  
**Imidophenylnaphthyl**, behaviour of, with chromic acid, III, 279  
**Iminazoic acid**. See *Azoimide*.  
 **$\beta$ -Iminazolyethylamine**, VII, 349  
**Imino-bases**, VII, 303  
**Imino urea**. See *Guanidine*.  
**Immedial black**, v, 377  
     FF extra, v, 564  
     V, N, v, 377  
     blue, v, 377  
     C, v, 378, 598  
     bordeaux, G, v, 380, 618  
     GF, v, 380  
     brilliant black, v, 562  
     5 BV, v, 568  
     green G extra, v, 572  
     brown B, v, 616  
     cutch BG, v, 620  
     dark brown D, v, 618  
     deep green G, v, 576  
     direct blue BB, v, 596  
     green GG extra, v, 576  
     indogens BCL, v, 596  
     indone, v, 378  
     R, v, 600  
     violet B, v, 608  
     maroon B (Cassella), v, 380  
     new blue G, v, 602  
     orange, v, 376  
     pure blue, v, 378  
     yellow GG, v, 586  
     olive 5 G, v, 614  
**Imperial red**, v, 192, 296  
     scarlet, v, 170  
     yellow. See *Aurantis*.  
**Indaconitine**, VI, 255, 256  
     salts and derivatives, of, VI, 269  
**Indalizarin R**, J, v, 350, 352  
     green, v, 350, 352  
**Indamine**, v, 326  
     GG, J, JOR, 2 R, 3 R, 6 R, v, 330  
     blue B, v, 590  
     for wool, v, 330  
     N, NB, v, 330  
     N extra, v, 330  
     NB extra, v, 332  
     WG, NR, v, 332

- Indamines, v, 310, 461  
 Indanthrene blue GC, GCD, v, 537  
   RC, v, 537, 598  
   brown, B, v, 538, 616, 620  
   claret, v, 536  
   copper, v, 535  
   R, v, 620  
   dark blue BO, v, 537  
   golden orange, v, 535  
   green B, v, 538  
   grey, v, 538  
   maroon, v, 538  
   olive, v, 538  
   orange RT, v, 535, 584  
   red, v, 536  
   violet R extra, v, 537, 606  
     RT, v, 537  
     yellow G, R, v, 535  
 Indazine, v, 590  
   M, v, 332, 461  
 Indaconitine, vi, 268  
 Indian mustard oil. See *Mustard oil, Indian*.  
   saffron. See *Turmeric*.  
   yellow, v, 139, 146; vii, 395  
 Indian-grass oils, iv, 303, 304  
 India-rubber, iv, 105  
   blown-oil substitute for, iv, 147, 150  
   brown substitute for, iv, 147, 150  
   composition of, iv, 107  
   devulcanised, iv, 133  
   estimation of, in ebonite, iv, 146  
     in raw rubber, iv, 110, 112; ix, 321  
     in vulcanised rubber, iv, 134; ix, 321  
   Penton, iv, 152  
   impurities in, iv, 107; ix, 322  
   latex, iv, 105; ix, 320  
     analysis of, iv, 106; ix, 320  
   *l*-methylinositol in, ix, 320  
   occurrence of, iv, 105  
   properties of, iv, 108  
   pyridine extraction of, ix, 322  
   raw, analysis of, iv, 110; ix, 321  
   recovered, iv, 134, 153  
   resins accompanying, ix, 320  
   Schneider's test for the quality of, iv, 114  
   substitutes, iv, 147  
   unvulcanised mixings, analysis of, iv, 115  
   vulcanised, iv, 115  
     acetone extraction of, iv, 123  
     analysis of, iv, 116, 121, 122; ix, 321  
     British admiralty test for, iv, 120  
     estimation of antimony in, iv, 142  
       of carbon in, iv, 137  
       of chlorine in, iv, 140  
       of india-rubber in, iv, 134; ix, 321  
       of oils in, iv, 124  
       of sulphur in, iv, 126, 138; ix, 323  
     mineral matter in, iv, 119, 138, 141; ix, 323  
     reclaiming of, iv, 153  
     specific gravity of, iv, 117  
     substitutes in, iv, 129  
     white substitute for, iv, 147, 150  
 Indican, v, 384  
   estimation of, iv, 385; ix, 427  
 Indicator, litmus as, v, 430  
   tumeric as, v, 415  
 Indicators, iii, 550  
   theory of, iii, 550  
   used in the estimation of alkaloids, vi, 181  
 Indigen D, F, v, 327  
 Indigo, v, 384, 463, 537; ix, 427  
   B, sulphur, v, 602  
   JRG, v, 598  
   MLB/2 B, 4 B, 5 B, 6 B, v, 537  
   MLB/T, v, 537  
   analysis of, v, 391; ix, 427  
   brown, v, 389  
   carmine, v, 455, 462, 467, 570, 588; ix, 453  
   comparative dyeing trials for, v, 392; ix, 436  
   constituents of, v, 386  
   detection of, v, 447  
     of logwood in the presence of, v, 408  
     in wines, i, 181  
   determination of colour effect of, ix, 439  
   disulpho acid, separation of, from the other  
     coal-tar colours in meat products, viii, 383  
   estimation of, v, 391; ix, 427.  
     by Brylinski's method, v, 393; ix, 428  
     on the fibre, v, 402; ix, 428, 436  
     of indigo-in in, by colourimetric tests,  
       v, 391  
     by extraction, v, 392; ix, 427  
     by oxidation processes, v, 393  
     by reduction tests, v, 399  
     by titanous chloride, v, 400  
   by Möhlau and Zimmerman's method, v, 402; ix, 428  
   in presence of starch, ix, 446  
   by Rawson's method, v, 393; ix, 427  
   examination of, v, 391; ix, 427  
   containing yellow colouring matter, v, 398  
   rich in indirubin, v, 396  
   gallanilic. See under *Gallanilic*.  
   preparation of, v, 384  
   pyrogene, v, 378, 600  
   red. See *Indirubin*.  
   substitute, v, 327  
   synthetic, v, 390  
   varieties of, v, 390  
   vat, v, 570  
   white, v, 387  
   yellow, v, 389  
 Indigotin, v, 386, 467  
   estimation of, v, 391, 402  
     by reduction tests, v, 399  
   sulphonic acids, v, 387  
 Indihumin, v, 389  
 Indirectin, v, 389  
 Indirubin, v, 385, 388  
   detection of, in urine, vii, 256  
   estimation of, v, 397  
   extraction of, v, 397  
 Indochromine RR, v, 602.  
   T, v, 316  
   (Sandoz), v, 358  
 Indochromogen S, v, 314, 316, 358  
 Indocytamine B, v, 598

- Indoin blue**, v, 590  
 2B, v, 570  
 R, v, 156, 332
- Indole**, vii, 252  
 ethylamine, vii, 351  
 in orange flowers, iv, 367  
 as a putrefaction product, vii, 352  
 and pyrole, distinction between, ix, 476  
 and skatole, distinction between, vii, 254
- Indole- $\alpha$ -amino-propionic acid**. See *Tryptophane*.
- Indophenin extra**, v, 327
- Indophenol**, v, 314, 455, 463, 467  
 blue, v, 588  
 detection of, v, 447  
 N, v, 311  
 reduced, v, 311  
 white, v, 311, 314
- Indophenols**, v, 310
- Indoxyl**, vii, 255  
 brown, v, 385
- Indoxyl-sulphuric acid**, vii, 255  
 detection of, in urine, vii, 255
- Induline**, v, 332, 463  
 3 B, 6 B, v, 327  
 black (Kalle), v, 332  
 (Kalle) spirit, v, 338  
 scarlet, v, 332  
 spirit-soluble, v, 467
- Indulines**, v, 325, 340, 588  
 detection of, v, 447  
 R, 6 B, v, 455  
 soluble, v, 327, 456, 462  
 sulphonated, v, 327  
 detection of, v, 445
- Infants' foods**, viii, 232
- Inflatin**, vi, 225
- Ingrain colours**, v, 118, 202, 372  
 maroon, v, 548
- Ink marks, chemical examination of**, v, 675
- Inks**, v, 669  
 blue, v, 670; ix, 463  
 cancelling, having an oil base, v, 679  
 materials used in, v, 686  
 coloured, v, 670; ix, 463  
 permanence of, to light, ix, 466  
 green, v, 670; ix, 464  
 invisible, v, 670  
 marking, v, 670  
 printing, v, 670; ix, 456  
 analysis of, ix, 457  
 composition of, ix, 456  
 dyes and lakes in, ix, 467  
 manufacture of, ix, 457  
 tests for, ix, 467  
 red, v, 670; ix, 463  
 resistance test, to sunlight and reagents, v, 673  
 rubber-stamp, v, 685  
 standard, v, 673  
 streak tests for, v, 672  
 writing, v, 669  
 black, examination of, v, 671  
 estimation of tannin in, ix, 468
- Inosinic acid**, viii, 290
- Inositol**, viii, 286
- Insecticides, estimation of nicotine in**, vi, 250
- Inulin, occurrence of laevulose in**, i, 373
- Inversion of sugars**. See *Sugars, inversion of*.
- Invert sugar**, i, 375  
 as an adulterant of honey, i, 384  
 analysis of, in brewing, ix, 7, 9  
 clarifying of, i, 311  
 detection of, in commercial honey, i, 385  
 estimation of, i, 375; ix, 24, 29  
 with Fehling's solution, i, 320  
 in presence of cane sugar, ix, 39, 42  
 large quantities of sucrose, i, 328  
 reducing power of, ix, 27, 39  
 table showing specific gravity of corresponding solutions of, and cane sugar, i, 295  
 typical analyses of, i, 376
- Invertase**, viii, 6  
 measurement of the activity of, viii, 8  
 preparation of, i, 314  
 use of, in estimating saccharose, ix, 46  
 in yeast, i, 211
- Iodeosin**. See *Tetraiodofluorescein*.  
 B, v, 296  
 G, v, 304
- Iodine, action of, on erythro-dextrin**, i, 420  
 detection of, in organic substances, i, 62  
 estimation of, in organic substances, i, 63  
 green, v, 259, 278, 453, 461, 472  
 reaction of, with erythro-dextrin, i, 428  
 with starch, i, 419  
 as a reagent for alkaloids, vi, 189  
 violet, v, 278
- Iodimetric method for the estimation of formaldehyde**, i, 261
- Iodised starch**, i, 419
- Iodoform, extraction of, with ether**, i, 282  
 commercial, i, 283  
 detection of picric acid in, i, 283  
 preparation of, i, 282
- Iodogallicin**, iii, 534
- Iodol**, vi, 150
- Iodophenol-*p*-sulphonic acids**, iii, 398
- Ipecacuanha alkaloids**, vii, 37; ix, 541  
 constitution of, ix, 544  
 estimation of, vii, 43, 44  
 percentage of, in commercial ipecacuanha, vii, 48  
 preparation of, vii, 41  
 reactions of, vii, 41  
 assay of, vii, 44  
 de-emetinised, vii, 49  
 root, vii, 43
- Ipecamine**, ix, 542
- Ipomic acid**, vii, 130
- Iris blue**, v, 346  
 violet, v, 328
- Irisamine G**, v, 304, 554
- Iron buff**, v, 580  
 acetates, i, 511  
 See also *Ferrous and ferric acetates*.  
 and cyanogen, compounds of, vii, 502  
 detection of, in cheese, viii, 258  
 in turkey-red oil, ii, 171  
 estimation of, in paper, i, 479  
 liquor, i, 511  
 meconates, vi, 414

Iron oxide, spent, estimation of naphthalene  
in, III, 246  
and quinine citrate, VI, 531  
and strychnine citrate, VI, 460  
Irone, IV, 190  
Isatin, V, 387  
Isatropic acid, VI, 293  
Isinglass, VIII, 618  
Isomeric bodies, determination of the structure of,  
I, 236  
Isoprene, IV, 163  
Isorcinol, III, 337  
Iva oil, IV, 445

## J

Jaborandi alkaloids, VII, 50; IX, 537  
Jaborine, VII, 52  
Jaft, reactions of, V, 49  
Jalap, VII, 130  
glucosides of, VII, 130  
orisiba, VII, 131  
resin, VII, 132  
tampico, VII, 131  
Jalapin, VII, 130  
Jalapinic acid, VII, 130  
Jamba oil, II, 69, 130  
Jama, estimation of benzoic acid in, IX, 284  
Janus black I, V, 562  
blue R, V, 594  
brown R, V, 614  
green G, V, 572  
red, V, 174  
Japaconitine, VI, 255, 256, 266  
salts and derivatives of, VI, 267  
Japan fish oil. See *Sardine oil*.  
Japan wax, II, 72, 191  
adulteration of, II, 194  
composition of, II, 192, 193  
detection of, in beeswax, II, 235  
fatty acids from, II, 193  
saponification of, II, 192, 193  
specific gravity of, II, 191  
and water, comparison of specific gravities of,  
II, 192  
Japanese isinglass. See *Agar-agar*.  
wood oil. See *Tung oil*.  
Jasmine oil, IV, 445  
Jateorrhizine, VI, 575  
Jaune acide, V, 138  
indien, V, 459  
Java beans, poisoning by, VII, 102  
Jellies' ultramicroscopic structure of, IX, 604  
Jervine, VII, 82, 84  
detection and estimation of, VII, 83  
sulphate, VII, 85  
pseudo-Jervine, VII, 82, 86  
Jesaconitine, VI, 255, 256, 273  
Jet black G, V, 165  
R, V, 165, 172, 558  
Jolles' estimation of acetone, I, 107  
Juglansin, VIII, 109  
Juniper berry oil, IX, 363  
oil, IV, 249, 250, 345, 446  
Jute fibre, microscopic appearance of, in paper, I,  
475

## K

Kæmpferia oil, IV, 446  
Kæmpferol, V, 389, 398  
Kasepräparat, VIII, 249  
Kairines, VI, 157  
Kairolines, VI, 157  
Kamala, V, 637  
Kambe wood, V, 431  
Kapok oil, IX, 135  
Katigen black T 3 B, BFC extra, V, 568  
deep black BG, V, 562  
yellow brown GG, V, 616  
Katigent-chrome blue 6 G, V, 598  
Kauri copal, IV, 52  
Keller's process for the estimation of alkaloids, VI,  
179  
in nux vomica, VI, 469  
reaction for digitoxin and digitalin, VII, 120  
Kephyr, VIII, 226, 231  
Keratin, VIII, 673  
from ox-horn, amino-acids formed by the hy-  
drolysis of, VIII, 20  
Keratins, VIII, 92  
Keratoids, VIII, 673  
Kermesin orange, V, 140  
Kerner test for cinchonidine in quinine sulphate,  
VI, 520  
Kerosene, III, 117, 119  
action of phenol on, III, 118  
American, III, 129, 130  
effect of temperature on the viscosity of,  
III, 149  
and Russian, comparison of illuminating  
power, III, 134  
test for distinguishing between, III, 136  
burning quality test for, III, 132  
by the Canadian method, III, 132  
by Redwood's apparatus, III, 133  
by Saybolt's apparatus, III, 132  
close test for, III, 121  
colour test, III, 130  
by the Stammer chronometer, III, 131,  
132  
by the Wilson chronometer, III, 130, 132  
crude and refined, detection of admixtures  
of, III, 136  
emulsions, III, 141  
estimation of soaps in, III, 142  
of sulphur in, III, 134  
fire tests and instruments required in differ-  
ent countries, III, 126, 127  
flash point, III, 120  
determination by Abel's closed oil tester,  
III, 122  
by the Abel-Penaky apparatus, III, 126  
by the New York closed oil-tester, III,  
124  
tests and instruments required in different  
countries, III, 126, 127  
fractional distillation of, III, 127  
illuminating power of, III, 133  
odour of, III, 130  
open test for, III, 121  
optical activity of, III, 135

**Kerosene**, refined, cause of turbidity in, III, 135  
 Russian, III, 129, 130  
 and American, comparison of illuminating power of, III, 134  
 test for distinguishing between, III, 136  
 effect of temperature on the viscosity of, III, 149  
 specific gravity determination, III, 129  
 test for, by the rate of consumption in similar lamps, III, 130  
 testing of, with sulphuric acid, III, 119  
**Ketchups**, estimation of benzoic acid in, III, 413; IX, 284, 285  
**Ketone blue B**, v, 592  
 4 BN, v, 278, 592  
**Ketones**, cyclic, IV, 190  
 of essential oils, IV, 189, 256  
 estimation of, in essential oils, IV, 231  
**Kiku oil**, IV, 446  
**Kinic acid**. See *Quinic acid*.  
**Kino**, v, 34  
**Kinoin**, v, 30  
**Kino-red**, v, 30  
**Kino-tannic acid**, v, 7  
**Kiton green N**, v, 574  
**Kjeldahl method** for the estimation of nitrogen, I, 59; VIII, 48  
 Arnold's modification of, I, 62  
**Kliphaut bark**, reactions of, v, 48  
**Klunge's test** for aloes, VII, 144, 146  
**Knapp's mercuric solution**, use of, in the estimation of dextrose, I, 337  
**Knoppert**, v, 35  
**Kobushi oil**, IV, 446  
**Koettstorfer's process** for the examination of fixed oils, IV, 230  
 determination of the saponification value of acids, II, 15, 377  
 saponification of oils, II, 14  
**Koko**, reactions of, v, 46  
**Kokum butter**. See *Goa butter*.  
**Kola**, VI, 680; IX, 532  
 bitter, VI, 683  
 false, VI, 683  
 male, VI, 683  
**Kolanin**, VI, 682  
**Kossel test** for purine bases, VII, 336  
**Koumiss**, VIII, 225, 230  
**Kräuter Käse**, VIII, 253  
**Kreis' phloroglucinol test** for the detection of peach-kernel and apricot-kernel oils in almond oil, II, 104  
**Kresol black BB**, v, 562  
**Krogene yellow R**, v, 586  
**Kruppelboom**, reactions of, v, 47  
 black B, kryogen, v, 564  
 brown, v, 616  
 RB, v, 620  
**Kunze's method** for the estimation of theobromine and caffeine, VI, 709  
**Kuro-moji oil**, IV, 446  
**Kusserow's method** for the determination of the fermenting power of yeast, I, 223  
**Kynurenic acid**, VII, 406; IX, 569

## L

**Labordin**, VI, 159  
**Laburnum**, alkaloid of, VII, 13  
**Laccainic acid**, v, 425  
**Laccase**. See *Oxydase*.  
**Lao-dye**, v, 424  
**Lacmoid**, v, 344  
 use of, as an indicator in the estimation of alkaloids, VI, 182  
**Lactalbumin**, VIII, 131, 140  
 estimation of, VIII, 138  
**Lactase**, VIII, 6  
 in yeast, I, 212  
**Lactates**, VII, 446  
 estimation of lactic acid in, VII, 448  
*d*-Lactic acid, VII, 449; IX, 582  
*l*-Lactic acid, VII, 449; IX, 582  
**Lactic acid**, anhydrous, VII, 432  
 British pharmacopœia requirements for, VII, 445; IX, 582  
 colour reactions of, I, 487  
 commercial, VII, 431  
 impurities in, VII, 443  
 valuation of, VII, 440  
 detection of, VII, 434; IX, 582  
 in organic tissues and extracts, VII, 45  
 estimation of, in the commercial acid, VII, 441  
 by Buchner and Meisenheimer's method, VII, 437  
 by Jerusalem's method, VII, 439  
 by Kuns' method, VII, 438  
 in lactates, VII, 448  
 by Moslinger's method, IX, 584  
 in organic tissues and extracts, VIII, 451; IX, 582  
 by Partheil's method, VII, 439  
 in urine, IX, 583, 584  
 ethylene, VII, 451  
 inactive, VII, 429  
 preparation of, VII, 429  
 properties of, VII, 432  
 salts of, VII, 446  
 separation of, from other organic acids, VII, 436  
 tests for, VII, 434; IX, 582  
 and titanin acid, compounds of, VII, 448  
 United States Pharmacopœia requirements for, VII, 444  
 acids, active, VII, 448; IX, 582  
 anhydride, VII, 432  
 estimation of, in commercial lactic acid, VII, 441  
**Lactide**, VII, 432  
**Lactogen**, full-cream, VIII, 218  
**Lactoglobulin**, VIII, 131, 140  
 estimation of, VIII, 138  
**Lactolin**, VII, 447  
**Lactometers**, VIII, 145  
**Lacto-milk-food**, VIII, 216  
**Lactosazone**, I, 365  
**Lactose**, I, 365; VIII, 197  
 action of, on ammoniacal silver nitrate, I, 365  
 on Fehling's solution, I, 362, 365



- Lactose**, action of, on mercurial reagents, I, 366  
 analysis of, VIII, 198, 203  
 detection of, I, 302  
   sucrose in, VIII, 202  
 effect of Barfoed's reagent on, I, 333  
 estimation of, I, 365; IX, 29, 57  
   in butter, II, 308  
   in cocoa, VI, 713  
   in condensed milk, I, 370; VIII, 214  
   in milk, I, 365; VIII, 157  
   by optical methods, I, 368  
   in presence of saccharose, IX, 62  
 factors for calculating the amount of copper  
   corresponding with the quantity of, I, 328  
 formation of mucic acid from, I, 376  
 hydrolysis of, I, 297  
 manufacture of, VIII, 197  
   by-products of, VIII, 202  
 pharmacopœial tests for, VIII, 200  
 specific rotation of, I, 365  
 tables for the estimation of, I, 367; IX, 58
- Lævuline blue**, V, 328
- Lævulose**, I, 373  
 commercial, estimation of, I, 374  
 detection of, in the presence of dextrose, I, 302  
 and dextrose, action of, on Fehling's solution, I, 374  
 estimation of, in mixtures, I, 375  
 estimation of, in the presence of other sugars, I, 373  
 methylphenylosazone, I, 375  
 reducing power of, I, 374; IX, 27  
 solution density of, IX, 19, 20  
 specific rotation of, I, 373  
 table showing specific gravity of solutions of, compared with corresponding solutions of cane sugar, I, 294
- Lafon's reaction** for digitoxin and digitalin, VII, 120
- Lake**, carmine, V, 423  
 pitch, composition of, III, 61, 62
- Lakes**, V, 623  
 examination of, V, 538
- Lallemantia oil**, II, 70, 151
- Lamb**, canned, VIII, 337  
 composition of, VIII, 270
- Lanacyl blue BB**, V, 594  
 navy blue B, V, 594
- Lanafuchsine**, BBS, V, 556
- Lancaster yellow**, V, 140, 143
- Lanolin**, II, 502; VIII, 683
- Lantana oil**, IV, 446
- Lanthopine**, VI, 354, 363, 367, 398
- Lanuginic acid**, VIII, 685
- Lapaconitine**, VI, 255, 277
- Larch turpentine**, IV, 76
- Larch-bark**, V, 46  
 analysis of, V, 67
- Larch-extract**, analysis of, V, 66  
 Hungarian, reactions of, V, 43  
 reactions of, V, 46
- Lard**, II, 72, 207, 317; IX, 178  
 bromine thermal value for, II, 319  
 composition of, II, 317
- Lard**, crystallisation of, II, 318, 321  
 detection of arachis oil in, II, 320  
   beef and other animal fats in, II, 321;  
   IX, 178  
   coconut oil in, II, 321  
   cottonseed oil in, II, 320, 321  
   maize oil in, II, 320  
   sesame oil in, II, 320, 321  
   vegetable oils in, II, 320  
 ethyl ester value for, II, 190  
 examination of commercial, II, 318  
 free fatty acids in, II, 319  
 grades of, in America, II, 317  
 iodine value for, III, 318  
 liquid fatty acids from, II, 319  
 oil, II, 72, 197  
   acidity of, II, 197  
   congealing point for, II, 199  
   constants for varieties of, II, 200  
   detection of, in almond oil, II, 103  
   in olive oil, II, 118  
   other oils in, II, 200  
   effect of blowing on, II, 367  
   flashing point of, II, 199  
   iodine value for, II, 199  
   Mauzene thermal value for, II, 198  
   oleo-refractometer values for, II, 198  
   saponification value for, II, 199  
   specific gravity of, II, 198  
   viscosity of, II, 198  
     effect of temperature on, III, 148  
   refractometer values for, II, 319  
   stearic acid from, II, 318  
   water in, II, 319
- Laudanidine**, VI, 36, 354, 363, 398
- Laudanine**, VI, 354, 361, 363, 367, 398
- Laudanosine**, VI, 354, 363, 367, 399  
 constitution of, VI, 361
- Laudanum**, VI, 429  
 Sydenham's estimation of morphine in, IX, 506
- Laurel oil**, II, 71, 182; IV, 446
- Laurent's acid**, VI, 119
- Lauric acid**, with its higher homologues, melting and solidifying points of mixtures of, II, 385
- Lauth's violet**, V, 353, 356, 454
- Lavender oil**, spike. See *Spike-lavender oil*.  
 oil's, IV, 244, 249, 250, 347, 446; IX, 363
- Lazuline blue R**, V, 596
- Lead acetate**, basic, I, 513  
 preparation of solution of, I, 308  
 acetates, I, 512  
 benzoate, III, 415  
 chromate, use of as a colouring matter for sweets, I, 358  
 cyanate, VII, 539  
 detection of, in commercial citric acid, I, 557  
   in organic substances, I, 75  
   in the presence of iron, I, 568  
 ethyl sulphate, I, 239  
 lactate, VII, 447  
 malate, I, 535  
 meconate, VI, 414  
 oleate, II, 412

- Lead**, picrate, III, 586  
 resinate, IV, 33  
 stearate, II, 400  
 succrate, I, 340  
 thiocyanate, VII, 548
- Leather**, adulterated, analysis of, V, 114  
 American, analysis of, IX, 415  
 analysis of, V, 105, 108, 112; IX, 411  
 brown, V, 163, 174, 363  
 detection of blood stains on, VIII, 572  
 estimation of sugar in, V, 101  
 Parker water absorption test of, V, 110  
 physical tests of, V, 109  
 yellow, V, 363
- Lecioplasma**, VIII, 216
- Lecithin**, estimation of, in eggs, IX, 620  
 in milk, VIII, 162  
 extraction of, from plants, VII, 283  
 preparation of, from yolk of egg, VII, 281  
 properties of, VII, 282
- Lecithins**, VII, 280
- Lecithoproteins**, VIII, 35
- Ledene**, IV, 253, 287
- Ledenol**, IV, 287
- Ledger bark**, VI, 480
- Ledum oil**, IV, 447
- Ledum-camphor**, IX, 343
- Lees**, I, 542  
 fermentation test for, I, 551
- Legal's nitroprusside test** for acetone, I, 105; VII, 402
- Legumelin**, VIII, 111
- Legumin**, VIII, 111
- Leguminous seeds**, proteins of, VIII, 110
- Lemon essences**, examination of, IV, 357  
 juice, I, 559, 560  
 adulteration of, I, 564  
 assay of, I, 563; IX, 110  
 fermentation of, I, 559  
 use of nitric acid for the adulteration of, I, 564  
 oil, IV, 244, 249, 250, 352, 447; IX, 365  
 adulteration of, IV, 353, 357; IX, 365  
 composition of, IV, 352  
 estimation of aldehydes in, IV, 234, 274  
 pinene in, IV, 356; IX, 365  
 table of constants for, IV, 355; IX, 365  
 thyme oil, IV, 447
- Lemon-grass oil**, IV, 244, 304, 307, 447; IX, 346  
 estimation of citral in, IV, 272, 308
- Lenigallol**, III, 539
- Lentil starch**, I, 412
- Leonhardi's method** for the measurement of the ink-resisting property of paper, I, 472
- Lepidine**, VI, 156
- Leucindophenol**, V, 456
- Leucine**, VII, 227  
 iso-leucine and valine, separation of, VIII, 25  
 separation of, from the hydrolysis products of proteins, VIII, 25
- Leucoindophenol**, V, 314
- Leucole brown B**, V, 538  
 dark green B, V, 538
- Leucoline**, VI, 151
- Leucosin**, VIII, 97  
 of barley, VIII, 104  
 of malt, VIII, 104
- Leunig's paper scales**, I, 467  
 testing machine, I, 468
- Levant sapotoxin**, VII, 127  
 wormseed oil, IV, 427, 459
- Licarhodol**, IV, 262
- Lichenin**, VIII, 621
- Lie tea**, VI, 639
- Lieben's iodoform test**, I, 229  
 for acetone, I, 105; VII, 401  
 for ethyl alcohol, I, 114
- Liebermann-Storch method** for the detection of palm oil in butter, II, 310, 316
- Liebig's extract of meat**, VIII, 305, 390, 398, 402, 420  
 analysis of, VIII, 424
- Light green**. See *Green, light*.
- Lignin**, estimation of, in crude fibre, I, 437
- Lignocelluloses**, I, 433  
 colour reaction of, I, 436
- Lignoceric acid** in arachis oil, II, 93
- Lime juice**, I, 559, 560  
 adulteration of, I, 564  
 analysis of, IX, 110
- Lime-nitrogen**, VII, 557
- Lime oils**, IV, 448; IX, 365
- Limonene**, IV, 168, 171, 172  
 and carvone, separation of, IV, 216  
 nitrolamines from, IV, 175, 176  
 nitrosochloride, IV, 174
- Linaloe oil**, IV, 448; IX, 366
- Linalol**, IV, 254, 258, 261  
 estimation of, in essential oils, IX, 328  
 specific gravity of, IX, 341
- d-Linalol**, identity of, with asarol, IX, 383
- Linalyl acetate**, detection of in essential oils, IX, 331
- Linen fibres**, microscopic appearance of, in paper, I, 474
- Ling-liver oil**, II, 221
- Lingué-tannin**, V, 7
- Linoleates**, II, 352
- Linoleic acid**, II, 350, 352  
 series of acids, II, 371, 374, 376
- Linolenic acid** of linseed oil, IX, 184  
 series of acids, II, 371, 374, 376
- Linoleum**, II, 362
- Linoxyn**, II, 35, 344; IX, 189
- Linseed**, VIII, 109, 110; IX, 181  
 cake, II, 326; IX, 182  
 ash from, II, 332  
 commercial, II, 323  
 oil, II, 70, 151, 323; IX, 180  
 absorption of phosphorus by, II, 353  
 acids, detection of, in commercial oleic acid, II, 409  
 action of nitric and nitrous acids on, II, 353  
 on sulphur, II, 353  
 adulteration of, II, 339; IX, 195  
 artists, II, 327  
 ash from, II, 332; IX, 187  
 blown, II, 362, 365  
 boiled, II, 353

- Linseed oil, boiled, adulteration of, II, 339, 356  
     analysis of, II, 358  
     constants for, III, 355  
     drying of, II, 355  
     insoluble bromides from, II, 355  
     iodine value of, II, 354  
     specific gravity of, II, 354  
     and unboiled, differentiation between, II, 357  
     uses of, II, 356  
 break test for, IX, 186  
 bromine value for, II, 336; IX, 189  
     effect of adulteration on, II, 342  
 composition of, II, 329; IX, 184  
     effect of boiling on, II, 346  
     exposure to air effect of, on, II, 345  
 constants of, II, 349  
 detection of in the boiled oil II, 355  
     cottonseed oil in, II, 341  
     fish oils in, II, 340; IX, 189  
     Japan wood oil in, II, 340  
     in rape oil, II, 130  
     rosin oil in, II, 341; IX, 195  
     in walnut oil, II, 353  
 driers for, II, 358  
 drying of, II, 35, 36, 343; IX, 192, 198  
     effect of light on, II, 348  
     storage on, II, 349  
     temperature on, II, 349  
     properties and iodine value, relationship between, II, 349  
 effect of adulteration on the characteristics of, III, 341  
     blowing on, II, 367; IX, 201  
     driers on, II, 347  
     storage on, IX, 196  
 estimation of rosin in, IX, 200  
 extraction of from paint, II, 328  
 fatty acids from, II, 330, 337  
     constants of, II, 350  
     insoluble, molecular equivalent of, II, 337  
 free fatty acids in, II, 333; IX, 187  
     effect of adulteration on, II, 343  
 film test, effect of adulteration, on II, 341  
 flash point of, II, 331  
 foots test for, IX, 186  
 group, II, 65, 70, 148; IX, 184  
 heat of combustion of, II, 339  
 insoluble bromides from, II, 336; IX, 189  
     bromide test for, II, 28  
     effect of adulteration on, II, 342  
 iodine value for, II, 334; IX, 188  
     effect of adulteration on, II, 342  
 linoleic acid from, II, 350  
 linolenic acid from, II, 352  
 linoxyn from, II, 344  
 lithographic varnishes from, II, 356  
 mucilage from, II, 328  
 oxidation of, II, 345, 346  
 ozone absorption of, II, 339  
 percentage obtained from various seeds, II, 324  
 preparation of from seed, II, 324; IX, 180  
 refining of, II, 326  
 refractive index of, II, 338; IX, 192  
 Linseed oil, refractometer value of effect of adulteration on, II, 342  
 rotation of, II, 338  
 saponification value for, II, 334  
     effect of adulteration on, II, 342  
 saturated acids of, IX, 185  
 solidification of, II, 331  
     effect of adulteration on, II, 341  
 solubility of, II, 332  
 soya bean oil in, II, 340  
 specific gravity of, II, 330, 336; IX, 187  
     effect of adulteration on the, II, 341  
 specification for, II, 343  
 substitutes for, II, 329  
 technical applications of, II, 327; IX, 184  
 unsaponifiable matter in, II, 333; IX, 188  
     effect of adulteration on, II, 342  
     values for, when extracted from paints, IX, 197  
 Lintner value of diastase, I, 136; VIII, 3  
 Linton's method for the fractional separation of the constituents of asphalt, III, 86, 89  
 Lipase, VIII, 291  
 Liqueurs, coloring matters, V, 655  
 Liquid waxes. See *Sperm-oil group of oils*.  
 Liquids, detection of metallic impurities in, I, 74  
     separation of oils from, in an emulsion, II, 6  
 Lithium benzoate, III, 414  
     carbonate in lithium citrate, I, 565  
     citrate, I, 565  
     commercial, I, 565  
     hydrogen urate, VII, 378  
     salicylate, III, 488  
 Lithofellic acid, VII, 416  
 Lithographic varnishes, II, 356  
 Litmus, V, 429  
     indicators, III, 552  
 Livettin, VIII, 92  
 Lobelia, tincture of, VI, 225  
 Lobeline, VI, 223; IX, 481  
 Löwenthal's method for tannin assay, V, 60; VI, 615  
 Loganin, VI, 468  
 Logwood, V, 403, 634, 637  
     blacks, V, 227, 558  
     blue, V, 588  
     colouring matter of, V, 403  
     detection of on the fibre, V, 407  
     in the presence of alizarin blue, gallocyanin or indigo, V, 408  
     in tea, VI, 630  
     in wines, I, 181  
     extracts, V, 405  
     specific absorption curves of, V, 440  
     test for alum in flour, I, 457  
     valuation of, V, 405  
 London blue, V, 252  
     method for the analysis of tartars, IX, 100  
 Loretine, III, 403; VI, 159  
 Lotahistone, VIII, 92  
 Lotusin, VII, 102  
 Lovage oil, IV, 448  
 Lovibond tintometers, V, 439  
 Lubricating greases, analysis of, III, 175, 181  
     determination of the consistency of, III, 176  
     flash point of, III, 176

**Lubricating greases**, determination of free acid in,  
     III, 176  
     melting point of, III, 175  
     soap content of, III, 177  
     water in, III, 179  
 lime soap, III, 180  
 Thurston tester for, III, 182

**Lubricating oils**, III, 142  
 action of on metals, III, 160  
 ash residue from, IX, 250  
 carbon residue test for, IX, 254  
     test for, IX, 250  
 classification of, III, 172  
 Cleveland open cup for, IX, 251  
 cold test for, III, 157  
 comparative values of, III, 144, 146  
 detection of aluminum palmitate and oleate  
     in, III, 163  
     mineral matters, in, III, 163  
 determination of flashing point, III, 158  
 gumming quality of, III, 159  
 loss of, by heating, III, 159  
 water in, IX, 253  
 drying properties of, III, 159  
 estimation of paraffin, IX, 257  
     sulphur in, IX, 248  
 evaporation test for, IX, 256  
 flash and fire test for, IX, 251  
 free acid in, III, 160, 174; IX, 253  
 inner friction of, III, 173  
 microscopical examination of, IX, 254  
 Pensky-Martens test for, IX, 252  
 precipitation test for, IX, 254  
 saponification value of, IX, 252  
 soap test for, IX, 252  
 specific gravity of, IX, 251  
 suitability of, for special purposes, III, 144  
 sulphur test for, IX, 253  
 viscosity of, III, 145, 173; IX, 251, 255  
     determination by Engler's viscosimeter, III,  
     154  
     Redwood's viscosimeter, III, 151  
     torsion viscosimeter, III, 154  
     Saybolt's viscosimeter, III, 156  
     of, effect of temperature on, III, 147. See  
     also *Mineral oil*.

**d-Lupanine**, VI, 228; IX, 482  
     dihydrobromide, IX, 482

**Lupanine**, inactive, VI, 228; IX, 482

**Lupeol**, II, 488

**Lupine alkaloids**, VI, 225; IX, 481  
     flakes, IX, 482

**Lupinidine**, VI, 227

**Lupinine**, VI, 226

**Lupins**, proteins of, VIII, 112

**Lupulin**, VII, 171

**Lupulinic acid**, VII, 165, 167

**Lupulotannic acid**, V, 7, 27

**Lustrocellulose**, VIII, 661

**Lutécienne**, V, 296

**Luteolin**, V, 411, 459

**Lutidine**, VI, 129

**Lutidinic acid**, VI, 147

**Lyaconine**, VI, 274

**Lycaconitine**, VI, 255; IX, 488

**Lycoc tonic acid**, VI, 275

**Lycoc tonine**, IX, 488

**Lysidine**, VII, 201

**Lysine**, VII, 261  
     estimation of, by Van Slyke's method, VIII, 82  
     separation of, from the products of protein  
     hydrolysis, VIII, 31

**Lysol**, III, 332  
     analysis of, III, 333

## M

**Macaroni**, VIII, 102  
     colouring matters in, V, 651

**Macassar oil**, II, 72, 194

**Macdougall's disinfecting powder**, III, 309

**Mace oil**, IV, 358, 448

**Maclurin**, V, 7, 409

**Madder**, V, 430, 550, 578

**Madia oil**, II, 70, 139

**Mafura tallow**, II, 71, 182

**Magdala red**, V, 325, 332, 463, 540  
     detection of, V, 447, 448

**Magenta**, V, 246, 461, 468, 472, 540  
     acid. See under *Acid*.  
     commercial, examination of, V, 248  
     detection of, V, 248, 445  
     in orchil and cudbear, V, 428  
     new, V, 278, 542  
     para, V, 282  
     roseine, V, 278  
     S, V, 249, 468

**Maggi's bouillon**, IX, 614

**Magnesium acetate**, I, 510  
     ammonium phosphate, detection of, in uri-  
     nary deposits, VII, 383  
     lactate, VII, 447  
     phosphate, detection of, in urinary deposits,  
     VII, 384  
     platinocyanide, VII, 534

**Maise**, I, 463  
     detection of in flour, I, 462  
     glutelin of, VIII, 107  
     oil, II, 70, 139  
     detection of, in olive oil, II, 118  
     composition of, II, 140  
     fatty acids from, II, 141  
     properties of, II, 140  
     proteins in, VIII, 106  
     starch, I, 413, 416

**Malabar tallow**. See *Piney tallow*.

**Malachite green**, V, 237, 239, 241, 278, 453, 461,  
     472, 570  
     G, V, 274  
     detection of, V, 445  
     test for blood, VIII, 524

**Malates**, I, 534. See also under *Parent substance*.

**Malic acid**, I, 533  
     action of heat on, I, 534  
     of hydriodic acid on, I, 534  
     with resorcinol, I, 487  
     estimation of, IX, 98  
     in presence of tartaric acid, IX, 108  
     separation of, from oxalic, tartaric and citric  
     acids, I, 534  
     and succinic acid, distinction between, IX, 99

- Mallet bark, IX, 396
- Malt, I, 133
- acidity of, I, 139
  - and barley, differences between, I, 133
  - roasted, determination of colour of, I, 142
  - extract of, I, 143
  - moisture of, I, 143
  - brown, analysis of, IX, 6
  - catalytic activity of, VIII, 15
  - chemical examination of, I, 134
  - cold water extract of, I, 138
  - crystal, analysis of, IX, 6
  - diastatic activity (Lintner value), I, 136
  - power of, VIII, 3; IX, 5
  - estimation of arsenic in, I, 146
  - of moisture in, I, 135
  - extract of, I, 134, 145
  - analyses of, I, 145
  - estimation of arsenic in, I, 147
  - valuation of, VIII, 689
  - grinding of, IX, 5
  - isolation of xanthine bases from, VII, 327
  - leucosin of, VIII, 104
  - liquors, I, 149
  - modification of, I, 139
  - nitrogenous constituents of, I, 139; VIII, 105
  - percentage of dry grains in, I, 140
  - physical examination of, I, 140
  - proteins in, VIII, 103
  - roasted, I, 142
  - analysis of, IX, 6
  - saccharification test, I, 139
  - sampling of, I, 134
  - Sinker test for, I, 140
  - substitutes, I, 143
  - estimation of arsenic in, I, 147
- wort, I, 140
- colour of, I, 135
  - estimation of apparent maltose and dextrin in, I, 141
  - of arsenic in, I, 147
  - reducing power of, I, 142
  - specific gravity of, I, 141
  - rotatory power of, I, 142
  - table showing degrees of gravity lost in, during fermentation, I, 153
- Malta vita, composition of, I, 464
- Maltase, VIII, 6
- identification of maltose by means of, I, 361
  - in yeast, I, 211
- Maltol, effect of, on the ferric chloride test for salicylic acid, III, 478
- Maltosazone, I, 365
- Maltose, I, 361
- action of, on Fehling's solution, I, 362
  - on Pavy's ammoniacal cupric solution, I, 362
  - yeast on, I, 362
  - anhydrous, table showing specific gravity of corresponding solutions of, and cane sugar, I, 295
  - birotation of, I, 362
  - cupric reducing power of, I, 570
  - detection of, I, 302
  - dextrin in the presence of, I, 302
  - small quantities of, I, 365
- Maltose, dextrose and dextrin, estimation of dextrin in a mixture of, I, 429
- and dextrose, distinction between, I, 365
  - effect of Barfoed's reagent on, I, 333
  - estimation of, I, 363; IX, 24, 29, 38, 53
  - small quantities of, I, 365
  - in plant extracts, IX, 65
  - factors for calculating the amount of copper to the corresponding quantity of, I, 328
  - fermentation of in the presence of dextrin, I, 300
  - hydrolysis of, I, 297, 361
  - identification of by means of maltose, I, 361
  - preparation of, I, 361
  - presence of, in leaves and barley, IX, 625
  - proportion of, in starch-sugar, I, 380
  - reducing power of, I, 362; IX, 27, 39
  - solution density of, IX, 20
  - specific rotation of, I, 362
- Malt-vinegar, I, 498
- Manchester brown, V, 163, 166
- EE, V, 170
  - yellow, V, 125, 145
- Mandarin, IV, 448; V, 137, 142, 459
- G, V, 139
  - orange oil, IV, 362, 451
- Mandelic acid, III, 506
- Mandelin's reagent, preparation of, VII, 92
- Mandragorine, VI, 291, 300
- Manganese brown, V, 610
- detection of, in tea, VI, 632
  - resinate, IV, 33
- Manganous benzoate, III, 415
- Mangosteen oil. See *Gos butter*.
- Mangrove, V, 39; IX, 395
- detection of, in quebracho, IX, 398
- Mangrove-bark, analysis of, V, 67
- extract, reactions of, V, 47
- Manila copal, IV, 52; IX, 310
- elemi, IV, 96; IX, 318
- Maple products, I, 388
- action of methyl alcohol on, I, 389
  - detection of adulteration of, I, 389
  - starch sugar in, I, 388
  - lead value of, I, 390
  - malic acid value of, I, 389
  - sugar. See *Maple products*.
  - syrup. See *Maple products*.
- Maracaibo balsam, IV, 83
- Maranham balsam, IV, 83
- Maranta arrowroot starch, I, 412, 415
- Marcitine, VII, 354
- Margarine, II, 313; IX, 166
- addition of butter to, II, 314
  - analysis of, IX, 174
  - detection of hardened fats in, IX, 173
  - ethylester value for, II, 190
  - regulations for, in various countries, II, 315
  - Reichert-Wollny, Reichert-Meissl, Polenske and Kirschner values for, II, 314; IX, 166
- Marine animal oils. See *Whale-oil group of oils*.
- blue, V, 252
  - B, V, 254
- Marinol acid blue R, V, 602
- Marjoram oil, IV, 448

- Marmalades**, estimation of salicylic acid in, IX, 303
- Marmé's reagent** for alkaloids, VI, 190
- Maroon**, acid, V, 249  
S. v. 249
- Maroons**, examination of, V, 510
- Mars red G**, V, 550
- Marsh tea oil**, IV, 448  
test for caramel in spirits, V, 656
- Marshall's paper testing machine**, I, 469, 470
- Marsh-Berzelius method** for the estimation of arsenic in malt, I, 146
- Martinon's tables** for the detection of dyes on silk, V, 511
- Martius' yellow**, V, 125, 457, 462
- Mason's essence of beef**, IX, 614
- Massecuités**, estimation of water in, I, 344
- Massory bark oil**, IV, 449
- Masterwort oil**, IV, 449
- Mastic**, IV, 12, 59
- Masticic acids**, IV, 5
- Masticolic acids**, IV, 5
- Masticonic acids**, IV, 5
- Masticoresenes**, IV, 6
- Maté**, VI, 641  
oil, IV, 449  
tannin, V, 7
- Matico-camphor**, IV, 210
- Matico-oil**, IV, 449
- Maturin**, VIII, 249  
balsam, IV, 83
- Maumené test** for fixed oils, II, 58
- Mauve**, V, 324, 461  
mauveine, V, 332
- Mauvéine**, V, 324, 454  
detection of, V, 445
- Mayer's reagent** for alkaloids, VI, 191
- Mazun**, VIII, 227
- Meadow-sweet**, essential oil of, I, 255  
oil, IV, 449
- Meat**, VIII, 261; IX, 607  
amino acids in, VIII, 290  
analysis of, VIII, 295  
bases, estimation of, in meat extracts, VIII, 408, 413  
canned, VIII, 330  
analyses of, VIII, 333  
metals in, VIII, 337, 340  
tin in, VIII, 337  
carnine in, VIII, 289  
chilled, VIII, 348  
cold-water extract of, VIII, 298  
composition of, VIII, 262, 277  
cooking of, VIII, 304  
creatine and creatinine in, VIII, 287, 302  
cured, analysis of, VIII, 373  
pickle for, VIII, 368  
composition of, VIII, 365  
estimation of starch in, VIII, 373  
curing of, VIII, 355, 362  
cuts of, VIII, 267  
decomposition of, VIII, 309; IX, 612  
definitions of, VIII, 261  
detection of benzoic acid in, IX, 281  
of glycogen in, VIII, 283
- Meat**, Eber's sulphide test for, VIII, 312  
enzymes of, VIII, 290  
estimation of benzoic acid in, IX, 285  
of dextrose in, VIII, 286  
of fat in, VIII, 296  
of glycogen in, VIII, 284  
of moisture in, VIII, 295  
of nitrogen in, VIII, 297, 300, 302  
of phosphorus in, VIII, 298  
of sulphur in, VIII, 297  
extracts of, VIII, 389; IX, 613  
analysis of, VIII, 401, 420  
bromine precipitation assay of, VIII, 421  
composition of, VIII, 396  
detection of yeast extracts in, VIII, 416  
estimation of bases in, VIII, 408, 413  
of boric acid in, VIII, 425  
of creatinine and creatine in, VIII, 410  
of gelatin in, VIII, 414  
of nitrogenous products of, IX, 625  
of peptones in, VIII, 409  
of xanthine bases in, VIII, 412  
manufacture of, VIII, 395  
non-nitrogenous constituents of, VIII, 424  
partition of nitrogen in, IX, 615  
varieties of, VIII, 398, 402  
fat, detection of changes in, VIII, 316  
rancidity in, VIII, 318  
frozen, VIII, 350, 352; IX, 613  
glycogen in, VIII, 281  
hot-water extract of, VIII, 302  
hypoxanthine in, VIII, 288  
identification of species of, VIII, 271  
inosinic acid in, VIII, 290  
juice, VIII, 299  
juices. See *Meat-extracts*.  
Liebig's extract of, VIII, 305, 390, 398, 402, 420, 424  
lipase in, VIII, 291  
mineral constituents of, VIII, 292, 294  
muscle extractives from, VIII, 281; IX, 607  
nitrogenous extractives of, VIII, 286  
poisonous, VIII, 319  
detection of, VIII, 324  
potted, VIII, 330  
precipitin, method for the analysis of, VIII, 271  
preservation of, VIII, 328  
with antiseptics, VIII, 351, 361  
products, detection of artificial colouring in, VIII, 382  
protase in, VIII, 290  
rations, composition of, IX, 619  
sampling of, VIII, 293  
smoking and drying of, VIII, 365  
spoilage of, VIII, 309  
structure and composition of muscle of, VIII, 276  
taurine in, VIII, 290  
uric acid and urea, VIII, 289  
xanthine in, VIII, 288
- Meconic acid**, VI, 411  
salts of, VI, 414
- Meconidine**, VI, 354, 363, 399
- Meconin** in opium, VI, 410
- Meconoisin**, VI, 411

- Meissl's method for the determination of the fermenting power of yeast, I, 222, 223  
 Mekong yellow G, v, 190  
     R, v, 196  
 Melaleuca, iv, 448  
 Melanogene blue, v, 380  
 Melanthrene B, v, 602  
 Meldola's blue, v, 341, 348, 461  
 Melibiase in yeast, I, 211  
 Melibiose, hydrolysis of, I, 297  
 Melilotic acid, III, 448  
 Melissa, iv, 448  
 Melissic acid in beeswax, II, 244  
 Melting point of organic substances, determination of, I, 16  
 Menhaden oil, II, 73, 224  
 Menispermine, VII, 164  
 Menthene, iv, 284  
 Menthol, iv, 254, 282; IX, 343  
     and thymol, separation of, iv, 290  
 Menthone, iv, 191, 282  
 Mercerine wool red, Y, v, 556  
 Mercerised cellulose, I, 432  
 Mercuric benzoate, III, 415  
     cyanide, VII, 477  
     fulminate, III, 586, 588; VII, 542  
     iodide, acid, preparation of, I, 368  
     nitrate, acid, preparation of, I, 368  
     salicylate, III, 489  
     thiocyanate, VII, 548  
 Mercury, detection and estimation of, in organic substances, I, 64  
     in explosives, III, 608  
     estimation of, in mercuric salicylate, III, 489  
     metallic, detection of, in explosives, III, 610  
     solutions, reactions of sugars with, I, 337  
 Mesoporphyrin, VIII, 555  
 Mesotartaric acid, I, 536  
     tartaric and racemic acids, separation of, I, 550  
 Metachrome brown B, v, 618  
 Metaldehyde, I, 267  
 Metals, detection of, in organic substances, I, 63  
     poisonous, occurrence in commercial organic products, I, 74  
 Metamine blue B, v, 342, 348  
     G, v, 342  
 Metanil yellow, v, 138, 141, 146, 580  
     S, v, 138  
 Metaphenylene blue, v, 590  
     B, v, 332, 461  
 Metaproteins, VIII, 35  
 Meteloidine, VI, 291, 301  
 Methacetin, VI, 104  
 Methæmoglobin, VIII, 539  
     spectrum of, VIII, 541, 690  
 Methaldehyde. See *Formaldehyde*.  
 Methene dichloride. See *Methylene dichloride*.  
 Methoxybenzoic acid, III, 507  
*m*-Methoxy-*p*-hydroxycinnamic acid, III, 448  
 $\beta$ -Methoxycynaphthalene. See  *$\beta$ -Naphthol methyl ether*.  
 Methyl aconitine, VI, 263  
     alcohol, I, 85; IX, 1  
     detection of, I, 88  
     in presence of ethyl alcohol, IX, 1.  
     estimation of, I, 91  
     in formaldehyde, I, 93  
     in presence of ethyl alcohol, I, 94; IX, 1  
     Hinkel test for, I, 90  
     Mulliken-Scudder test for, I, 88  
     Sanglé-Ferrière-Cuniasse test for, I, 89  
     Trillat test for, I, 89  
     United States Pharmacopœia test for, I, 88  
     Voisenet test for, I, 90  
     alkali blue, v, 253, 270  
     anthranilate, iv, 367  
     detection and estimation of, in essential oils, iv, 363  
     benzene. See *Toluene*.  
     benzoate, III, 415  
     blue, v, 251, 280  
         M, v, 255  
         for silk, MLB, v, 254, 272  
         water soluble, v, 272  
     carbinol. See *Ethyl alcohol*.  
     catecholate. See *Guaiacol*.  
     cinnamate, III, 438  
     crotonic acid. See *Tiglic acid*.  
     ether, I, 231  
     green, v, 259, 280, 453, 461, 472, 570  
         detection of, v, 445  
     orange v, 138, 141, 144, 458  
         indicators, III, 552; VI, 182  
     pentoses, estimation of, I, 403  
         and pentosans, estimation of a mixture of, I, 403  
     phenate. See *Anisole*.  
     quinolones, VI, 155  
     salicylate, III, 492; IX, 305  
         commercial, III, 495  
         estimation of, in foods and drugs, III, 49  
     salicylic acid, III, 507  
     violet, v, 461, 472, 604  
         B, v, 256, 280  
         2 B, v, 256, 280  
         6 B, v, 258, 272, 280, 454, 606  
         7 B, v, 258, 272  
         R, v, 454  
         V 3, v, 256, 280  
         detection of, v, 445  
 Methylacetanilide, VI, 86  
 Methyl-*m*-amido-*p*-hydroxy-benzoate, III, 502  
 Methyl-*p*-amido-*m*-hydroxy-benzoate, III, 502  
 Methylamine, VI, 11, 12; VII, 345  
 Methylamines and ammonia, separation and estimation of, VI, 18  
 Methylammonium chloride, VI, 13  
     picrate, VI, 13  
     platinichloride, VI, 13  
 Methyl-aniline, VI, 88, 91  
     estimation of, VI, 92  
     green, v, 259  
     nitrosame, VI, 89  
     violet, v, 256  
 Methyl-anthracene, III, 265  
     behaviour of, with chromic acid, III, 279



- Methylated chloroform**, I, 277  
   ether, I, 231  
   finish, I, 114  
   spirit, estimation of, in tinctures, I, 95  
     use of, for the preparation of spirit of  
       nitrous ether, I, 246  
   of wine, I, 112  
**Methyl-benzaconine**, VI, 265  
 $\alpha$ -**Methyl-camphor**, IV, 210  
**Methyl-chavicol**, IV, 255, 291  
**Methyl-coniine**, VI, 216  
 $m$ -**Methylcytisine**, IX, 535  
 $r$ -**Methyl-2-6-dioxy-purine**. See *Methyl-xanthine*.  
**Methyl-diphenylamine**, VI, 97  
   blue, V, 280  
**Methylene blue**, V, 353, 455, 461, 467, 472, 588  
   B, V, 354, 356  
   BB, BG, V, 354  
   detection of, V, 445  
   extra D, V, 354  
   ID, V, 354  
   dichloride, I, 281  
     and chloroform, distinction between, I, 281  
   digallic acid, III, 534  
   gallate, III, 534  
   green, V, 358, 445  
   G, V, 356  
   grey, V, 316  
   terchloride. See *Chloroform*.  
   violet, RRA, 3 RA, V, 334  
**Methyl-eosin**, V, 296, 297, 540  
**Methyl-ethyl acetic acid**, I, 524  
   pyridines, VI, 144  
**Methyl-eugenol**, IV, 255, 291, 294  
**Methyl-glycocoll**. See *Sarcosine*.  
**Methyl-glycocyamidine**. See *Creatinine*.  
**Methyl-glycocyamidine**. See *Creatine*.  
**Methyl-granatonine**, VI, 231  
**Methyl-guanidine**, VII, 306  
   as a putrefaction product, VII, 352  
**Methyl-guanidine-acetic acid**. See *Creatine*.  
   anhydride. See *Creatinine*.  
**Methyl-heptenone**, IV, 190  
**Methyl- $n$ -heptylketone**, IV, 190  
**Methyl-hydrazine**, VI, 30  
**Methylhydroxybenzenes**. See *Cresols*.  
**Methyl-indole**. See *Skatole*.  
**Methyl-lupinine**, VI, 227  
 $\alpha$ - and  $\beta$ -**Methylnaphthalenes**, III, 250  
**Methyl-nonylketone**, IV, 189  
**Methyl-pelletierine**, VI, 231; VII, 50  
**Methyl-phenacetin**, VI, 104  
**Methylphenyl- $\alpha$ -naphthylamine**, VI, 116  
**Methyl-phloxin**, V, 302  
**Methyl-isopropyl-phenols** in essential oils, IV,  
   287  
**Methylpurines**, VII, 321  
   estimation of, in urine, VII, 340  
**Methyl-pyridines**, VI, 142  
**Methyl-pyrroles**, VI, 149  
**Methyl-thiophen**, III, 211  
**Methyl-xanthine**, VII, 322, 338  
**Mew oil**, IV, 449  
**Microspectroscope**, I, 40  
**Migrainine**, VI, 47  
**Mikado brown**, B, 3 GO, and M, V, 132  
   G, V, 612  
   golden yellows, V, 124  
   orange, V, 132, 462  
   4 R, R, V, 582  
   yellow, V, 132  
**Milchlin**, VIII, 218  
**Milk**, VIII, 139  
   action of formalin on, VIII, 125  
   rennet-enzyme on, VIII, 125  
   adulteration of, VIII, 164  
   albumin, VIII, 131, 140  
     estimation of, VIII, 138  
   aldehyde number of, VIII, 154  
   analysis of, by general calculation methods,  
     VIII, 163  
   Babcock's formula for, VIII, 163  
   bacteriological examination, VIII, 176  
   boiled and unboiled, test to distinguish be-  
     tween, VIII, 14  
   Bonnet's test for formaldehyde in, VIII, 171  
   Buddeised, VIII, 222  
   butter, VIII, 195  
   chocolate, VI, 695, 705  
   colouring matter in, V, 659; VIII, 169  
   composition of, VIII, 141  
   condensed, VIII, 206  
     analysis of, VIII, 210, 212  
     estimation of saccharose in, IX, 56  
     of sugars in, I, 370; IX, 597  
     sweetened, VIII, 209  
   detection of abrastol in, III, 260; VIII, 175  
   of the addition of water to, VIII, 164  
   of annatto in, VIII, 169  
   of benzoates in, VIII, 173  
   of benzoic acid in, VIII, 173, 411; IX, 280  
   of borates in, VIII, 174  
   of calcium saccharate, VIII, 167  
   of formaldehyde in, I, 259; VIII, 171  
   of gelatin in, VIII, 166  
   of hydrogen peroxide in, VIII, 173  
   of nitrites in, VIII, 172  
   of saccharin in, III, 433  
   of salicylates in, VIII, 173  
   of salicylic acid in, III, 477  
   of sodium carbonate and sodium hydro-  
     gen carbonate in, VIII, 174  
   of sucrose in, VIII, 166  
   of tyrotoxin, VII, 355  
   determination of the specific gravity of, VIII,  
     144  
   diabetic, VIII, 218  
   dried, VIII, 235  
     analysis of, VIII, 239; IX, 600  
   effect of hydrogen peroxide on, VIII, 690  
   estimation of the acidity of, VIII, 160  
     of albumin in, VIII, 155  
     of amino-derivatives in, VIII, 157  
     of ammonium compounds in, VIII, 157  
     of benzoic acid in, III, 413; IX, 284  
     of borates, VIII, 174  
     of casein in, VIII, 131, 155; IX, 596  
     of citrates in, by Denige's method, VIII,  
       161  
     Desmoulière's method, VIII, 160

- Milk, estimation of fat in, by Adam's method, VIII, 148  
 by Babcock method, VIII, 149, 151  
 by the centrifugal methods, VIII, 150  
 by the Gerber method, VIII, 152  
 by the Leffmann-Beam method, VIII, 150  
 by the Rôse-Gottlieb method, VIII, 151  
 by Wanklyn's method, VIII, 148  
 of formaldehyde in, I, 260; VIII, 172  
 of lactose in, I, 368; VIII, 157  
 of modified proteins in, VIII, 157  
 of original solids in decomposed samples, VII, 177  
 of proteins in, by the Ritthausen method, VIII, 153  
 of salicylic acid in, III, 485  
 of sugar in, I, 365  
 of total proteins in, VIII, 153  
 of total solids in, VIII, 147  
 fermented, VIII, 223  
   analysis of, VIII, 231  
 Fleischmann's formula for, VIII, 163  
 galafer, VIII, 216  
 heated, detection of, by Arnold's method, VIII, 168  
   benzidine method, VIII, 168  
   Dupouy's method, VIII, 168  
 Hehner's test for formaldehyde in, VIII, 171  
 homogenised, VIII, 220  
 humanised, VIII, 215  
 organic pollution of, VIII, 175  
 pasteurisation of, VIII, 143  
 peptonised, VIII, 218  
 polarimetric estimation of, VIII, 158  
 preservation of, for analysis, VIII, 176  
 preservatives in, VIII, 170  
 products, VIII, 143, 179; IX, 597  
 proteins, VIII, 113, 140; IX, 595  
   estimation of, VIII, 132, 153  
   in condensed milk, VIII, 213  
   peptonised milk, VIII, 219  
   nomenclature of, VIII, 113  
 removal of proteins from, for the estimation of lactose, I, 366  
 Richmond's formula for, VIII, 163  
 separation of cream from, VIII, 182  
 separator slime from, VIII, 183  
 skim, VIII, 186  
   condensed, VIII, 210  
 sour, VIII, 223  
 specially treated, VIII, 222  
 sterilised, VIII, 221, 143  
 sugar. See *Lactose*.  
   molasses, VIII, 203  
   thickening agents used for, VIII, 166  
 Milk-globulin, VIII, 131, 140  
   estimation of, VIII, 138  
 Milling blue, v, 334  
   green S, v, 572  
   orange, v, 174  
   R, v, 620  
   red R, v, 546  
   scarlet B, v, 556  
   yellow, v, 140, 143, 158  
   O, v, 580  
 Millon's reagent, reactions of, with phenols, III, 296  
   for proteins, VIII, 38  
 Mills and Snodgrass' process for the estimation of olefines in liquid hydrocarbons, III, 4  
 Mimosa, v, 39, 372, 582  
   bark, reactions of, v, 43, 48  
 Mimotannic acid, v, 27  
 Mineral burning oils, III, 117  
   varieties of, III, 118  
 naphtha, III, 111  
 oil, III, 163  
   de-blooming agents for, III, 170  
   detection of caoutchouc in, III, 171  
   of  $\alpha$ -nitronaphthalene in, III, 170  
   of rosin oil in, III, 160, 174  
   in rosin oil, IV, 45  
   estimation of fatty oils in, III, 169  
   of rosin oil in, III, 174; IV, 45  
   examination of, III, 165  
   flash point of, III, 158  
   fluorescence of, III, 164  
   heavy, examination of, III, 172  
   Pensky-Martens test for, III, 167  
   specific gravity of, III, 165  
   tests for, III, 168  
   Thurston's tester for, III, 171  
 oils, acid tests for, III, 170  
   action of alkali on, III, 164  
   of bromine on, III, 164  
   behaviour of castor oil with, II, 163  
   cold test for, III, 166  
   colour of, III, 165  
   determination of specific gravity of, IX, 247  
   estimation of asphalt content of, IX, 246  
   of hard asphalt in, IX, 249  
   of paraffin in, IX, 257  
   of sulphur in, IX, 247  
   in turpentine, IV, 417  
 sperm oil, III, 118  
 Mint oil, mountain, IV, 450  
 Modulus of expansion of oils, II, 50  
 Moëllon. See *Dégras*.  
 Moisture, absorption of, by the Hill calcium chloride tube, I, 57  
   estimation of, in organic substances, I, 64  
 Molasses, I, 355  
   as an adulterant of honey, I, 384  
   analysis of, I, 356  
   assay of, I, 352  
   beet, analysis of, IX, 47  
   presence of optically active substances other than sugar in, I, 357  
   cane, analysis of, IX, 46  
   sugar, fermentation of, I, 357  
   composition of, I, 355  
   estimation of ash in, I, 356  
   of dextrose in, I, 356  
   of organic matter not sugar, I, 356  
   of sucrose in, I, 357; IX, 45  
   of sugars in, I, 357  
   of tin in, I, 348  
   of water in, I, 344, 356  
 milk sugar, VIII, 203  
   presence of vanillin in, I, 356  
   production of, I, 355

- Moleschott's test for cholesterol**, II, 483  
**Molloy process for gold extraction**, VII, 501  
**Monamines**, VI, 2, 10; VII, 195  
**Monamino-acids, estimation of**, VII, 262  
**Monarda oil**, IV, 449  
**Monochrome brown G**, V, 614  
**Monohydric phenols**. See *Phenols, monohydric*.  
 **$\alpha$ -Monopalmitin**, II, 397  
**Monosaccharides**, I, 372  
     properties of, I, 286, 287  
**Morawaki's test for rosin oil**, IV, 42  
**Morin**, V, 409  
**Morintannic acid**, V, 7, 409  
**Morphine**, VI, 354, 365, 374; IX, 497  
     acetate, VI, 378; IX, 497  
     basic associates of, VI, 395  
     and colchicine, distinction between, VII, 5  
     constitution of, VI, 355  
     detection of, VI, 379; IX, 497  
     in cases of poisoning, VI, 435; IX, 508  
     estimation of, VI, 383, 433; IX, 497, 504  
     by British Pharmacopoeia method, IX, 502  
     colorimetrically, VI, 433; IX, 497  
     in compounds, IX, 506  
     in opium, VI, 417; IX, 504  
     in paregoric, VI, 431  
     in pills, IX, 507  
     hydriodide, VI, 377  
     hydrochloride, VI, 377  
     meconate, VI, 378  
     nitrate, IX, 497  
     in opium, VI, 408; IX, 504  
     and pseudo-morphine, distinction between, VI, 437  
     and quinine, separation of, VI, 511  
     reactions of, VI, 379  
     salts of, VI, 376; IX, 497, 501  
     solubility of, VI, 363, 374  
     in acetone and water, IX, 496  
     sulphate, VI, 378; IX, 497, 501  
     tartrate, VI, 378  
     toxicology of, VI, 434; IX, 508  
**pseudo-Morphine**, VI, 354, 363, 404  
     constitution of, VI, 357  
     and morphine, distinction between, VI, 437  
**Morphine-narcotine meconate**, IX, 503  
**Morphothebaine**, VI, 406  
**Mosquera beef meal**, IX, 614  
**Mountain mint oil**, IV, 450  
**Mouth-washes, analysis of**, III, 498  
**Mucic acid, formation of, from lactose and galactose**, I, 376  
     preparation of, I, 376  
     from gums, I, 441  
**Mucina**, VIII, 92, 627  
**pseudo-Mucina**, VIII, 92  
**Mucocelluloses**, I, 434  
**Mucoids**, VIII, 92  
**Mugwort oil**, IV, 450  
**Mulford's predigested beef**, IX, 614  
**Muller's bursting strain paper testing machine**, I, 471  
**Mulliken-Scudder test for methyl alcohol**, I, 88  
**Murdock's liquid food**, IX, 614  
**Muscarine**, V, 342, 350, 461, 604; VII, 271, 284  
     detection of, V, 445  
     *so*-Muscarine, VII, 271, 286  
**Muscle extractive, detection of inositol in**, IX, 608  
     estimation of glycogen in, IX, 608  
     of lactic acid in, IX, 608  
     extractives, VIII, 280  
     glycogen in, IX, 607  
     nitrogenous, IX, 609  
     phosphorus compounds in, IX, 611  
     proteins of, VIII, 279  
     structure and composition of, VIII, 276  
**Musk root oil**, IV, 450  
**Mustard, adulteration of**, VII, 112  
     commercial, analysis of, VII, 106  
     constituents of, VII, 103  
     French, VII, 115  
     glucosides of, VII, 103  
     oil, IV, 450; IX, 134  
     black, II, 69, 120; IX, 134  
     detection of, in butter, II, 316  
     estimation of allyl thiocarbimide, IV, 300  
     hedge, detection of, in rape oil, II, 130  
     indian, II, 69, 121  
     properties of, II, 120  
     volatile, VII, 110  
     estimation of, VII, 108  
     white, II, 69, 120; IX, 134  
     prepared, examination of, VII, 114  
     seed, microscopic structure of, VII, 103  
**Mustard-husk oil**, II, 120  
**Mutarotation**, I, 315  
**Mutton, canned**, VIII, 337  
     composition of, VIII, 270  
     fat, II, 72, 207  
     tallow, II, 208  
**Mydrasine**. See *Atropine methobromide*.  
**Mydriatic alkaloids**, VI, 289  
     assay of, in belladonna root and preparations, VI, 314  
     in belladonna, VI, 312  
     in datura, VI, 319  
     in hyoscyamus, VI, 316  
     plants yielding, VI, 289, 311  
     scopolia, VI, 320  
     toxicological detection of, VI, 309  
**Myoetonine**, VI, 255, 273, 275; IX, 488  
**Myogen**, VIII, 92  
**Myosin**, VIII, 92  
**Myosinogen**, VIII, 92, 279  
**Myrabolans**, V, 36  
     analysis of, V, 67, 102  
     reactions of, V, 42, 49  
**Myrcene**, VII, 174; IX, 324  
**Myrcia oil**, IV, 450  
**Myricin in beeswax**, II, 244  
     estimation of, II, 247  
**Myricyl alcohol**, II, 244  
**Myristic acid with its higher homologues, melting and solidifying points of mixtures of**, II, 385, 386  
**Myristicin in mace oil**, IV, 359  
**Myrosin**, VII, 105  
**Myroxoresene**, IV, 6

Myrrh, IV, 98; IX, 318

herabol, IV, 98

oil of, IV, 103; IX, 318

tests for, IV, 99

tincture of, IV, 102

varieties of, IV, 98

Myrtle, V, 463

oil, IV, 450

wax, II, 72, 194

Mystin, detection of, in cream, VIII, 192

## N

Nankin, V, 363

Naphtamine brown R, 2 B, V, 616

Naphtha, III, 111

burning, III, 222

carbureting, III, 222

coal-tar, III, 220

commercial. See *Naphtha, coal-tar, crude*.

crude, III, 198, 221

assay of, III, 225, 235, 236

bulb-tube test distillation for, III, 233

dehydration of, III, 225

detection of carbon disulphide in, III, 226

distillation of, III, 239

distilling points of varieties of, III, 235

fractional distillation of, III, 229

and once-run comparison of distillation of, III, 236

petroleum spirit and shale naphtha, comparison between III, 116

retort test distillations for, III, 230

once-run, III, 221

assay of, III, 235, 240

distillation of, III, 236

shale. See *Shale naphtha*.

solvent, III, 222

Napthalene, III, 243, 266, 268; IX, 266

acid black, 4 B, V, 564

behaviour of, with benzal chloride, III, 280

chromic acid, III, 278

blue G, V, 588

chemical properties of, III, 243

commercial, III, 247, 250

compound of, with picric acid, III, 275

crude, III, 248

detection of, III, 244

phenol in, III, 250

dihydride, III, 250

effect of solvents on, III, 274

estimation of, III, 245; IX, 266

in carbolic oil, III, 247

in coal-gas, III, 245; IX, 266

in the commercial product, III, 250

in creosote oil, III, 374

sheep dips, III, 328

in middle oil, III, 247

in phenol, III, 247

by the picrate method, IX, 236

in spent oxide, III, 246; IX, 268

and naphthols, distinction between III, 254, 255

oils, III, 250

physical properties of, III, 243

Napthalene, pure, III, 249

reactions of, with metallic chlorides, III, 277

red, V, 332

salts, III, 248

sensitiveness of, to air and light, III, 250

sulphonic acids, III, 251

tetrahydride, III, 250

Napthalidinic acid, VI, 119

Napthazarin S, V, 218

Napthazine blue, V, 334

Napthenes, III, 201; IX, 236

Napthine brown  $\alpha$ ,  $\beta$ , V, 156

Napthionic acid, VI, 119

red, V, 148

$\alpha$ -Napthionic acid, VI, 117

Napthol dark green G, V, 572

Napthol green, V, 570

B, V, 130, 131, 462, 466

$\alpha$ -Napthol commercial, III, 255

estimation of, in the presence of large quantities of  $\beta$ -napthol, III, 256

yellow, V, 122, 125, 142, 576

detection of, in napthol yellow S, V, 128

estimation of, V, 480

S, V, 122, 128, 462, 466, 576; IX, 453

separation of, from the other coal-tar colours in meat products, VIII, 383

$\beta$ -Napthol black, V, 164, 558

B, V, 558

3 B, V, 165, 558

6 B, V, 165, 172, 558

4 R, V, 165

blue, V, 311

blue B, V, 342

blue-black, V, 172

B N, V, 564

commercial, III, 255

detection of, in butter, II, 311, 312

foods, III, 257

estimation of, IX, 269

by the iodometric method, III, 258

picric acid method, III, 258

ethers, III, 259

ethyl ether, III, 259

methyl ether, III, 259

orange, V, 139, 459

pharmacopoeia requirements for, IX, 269

sulphonic acids, III, 259

test for acetaldehyde, I, 266

for formaldehyde, I, 257

yellow, V, 142

$\alpha$ -Napthol-azo-napthalene, V, 136

$\beta$ -Napthol-azo-benzene, V, 136

$\alpha$ - and  $\beta$ -Napthols, III, 252

behaviour of, with tetravalent titanium, IX, 272

detection of, in cream, VIII, 192

distinctions between, III, 253

and napthalene, distinction between, III, 254, 255

sulphonic acids, III, 401

Napthomelan, SB, V, 568

Napthyl blue, V, 325, 334, 592

2 B, V, 188

red, V, 334

- Naphthyl, violet, v, 325, 334, 606  
 $\alpha$ -Naphthylamine, v, 205; vi, 112  
 $\beta$ -Naphthylamine, vi, 113  
 Naphthylamine Black, D, v, 165, 172, 558  
     black, v, 165  
     brown, v, 148, 610  
 $\alpha$ -Naphthylamine disulphonic acids, vi, 122  
     monosulphonic acids, vi, 117  
 $\beta$ -Naphthylamine disulphonic acids, vi, 123  
     monosulphonic acids of, 120  
 Naphthylamine trisulphonic acids, vi, 123  
     yellow, v, 125  
 $\alpha$ - and  $\beta$ -Naphthylamines, distinctions between,  
     vi, 111  
 $\alpha$ -Naphthylaminedisulphonic acid, vi, 122  
 $\beta$ -Naphthylaminedisulphonic acid, vi, 123  
 1-Naphthylamine-3:6-disulphonic acid, vi, 122  
 1-Naphthylamine-3:8-disulphonic acid, vi, 122  
 1-Naphthylamine-4:6-disulphonic acid, vi, 122,  
     125  
 1-Naphthylamine-4:7-disulphonic acid, vi, 122,  
     125  
 1-Naphthylamine-4:8-disulphonic acid, vi, 123,  
     125  
 2-Naphthylamine-3:7-disulphonic acid, vi, 123  
 2-Naphthylamine-6:8-disulphonic acid, vi, 123,  
     125  
 1-Naphthylamine-2-sulphonic acid, vi, 117  
 1-Naphthylamine-3-sulphonic acid, vi, 119  
 1-Naphthylamine-4-sulphonic acid, vi, 119, 125  
 1-Naphthylamine-5-sulphonic acid, vi, 119  
 1-Naphthylamine-6-sulphonic acid, vi, 120  
 1-Naphthylamine-7-sulphonic acid, vi, 120, 125  
 1-Naphthylamine-8-sulphonic acid, vi, 120, 125  
 2-Naphthylamine-5-sulphonic acid, vi, 120, 125  
 2-Naphthylamine-6-sulphonic acid, vi, 121, 125  
 2-Naphthylamine-7-sulphonic acid, vi, 121, 125  
 2-Naphthylamine-8-sulphonic acid, vi, 121, 125  
 Naphthylaminesulphonic acids, analysis of, vi,  
     124  
 Naphthylene blue R, v, 590  
     in crystals, v, 341  
     red, v, 170, 548  
 Naphthylene-diamines, vi, 117  
 Naphtindone BB, v, 594  
 Naphtogene blue 2 R, v, 598  
 Narcein, v, 140, 143  
 Narceine, vi, 354, 364, 367, 399  
     constitution of, vi, 360  
     test for, vi, 366  
 Narcophine, ix, 503  
 Narcotine, vi, 354, 364, 400  
     constitution of, vi, 357  
     detection of, in morphine salts, ix, 501  
     formation of, in opium-poppy, ix, 477  
     meconate, vi, 402  
     in opium, vi, 409  
     solubility of, in acetone and water, ix,  
         496  
 Natal aloes, aloin from, vii, 140  
 Natal arrowroot starch, i, 412  
 Nataloins, vii, 139, 140  
 Nativelle's crystallised digitalin, vii, 119  
 Navy blue B, v, 272  
     BW, v, 602  
 Neatsfoot oil, ii, 72, 200  
     adulteration of, ii, 201  
     composition of, ii, 200  
     constants for, ii, 201  
     effect of temperature on the viscosity of  
         iii, 148, 149  
 Neosote, iii, 363  
 Neptune green SG, v, 574  
 Neradol D, ix, 409  
 Nerol, iv, 254, 262, 367; ix, 341  
 Neroli oil. See *Orange-flower oil*.  
     Chinese, iv, 368  
 Nerolidol, iv, 367; ix, 342, 343  
 Nerolin, iii, 259  
 Neuridine, vii, 352  
 Neurine, vii, 274  
     and choline, distinctions between, vii, 275  
     as a putrefaction product, vii, 352  
 Neutral blue, v, 334, 461, 590  
     red, v, 321, 334, 548  
     violet, v, 320, 334, 461  
     wool blue R (Kalle), v, 280  
 Neutraline, ix, 120  
 Nevralteine, test for, vi, 48  
 New blue, v, 588  
     B, v, 342, 348  
     (Cassella), v, 341  
     detection of, v, 445  
     G, v, 342, 348  
     R, v, 341, 348  
 cocin, v, 150  
 fast blue for cotton, v, 341  
     green 3 B, v, 242, 284  
 fuchsin process of Meister, Lucius and  
     Brüning, v, 245  
 fuchsine, v, 278  
 green, v, 241, 278  
 grey, v, 314  
 magenta, v, 278, 542  
 methylene blue GG, v, 350, 461  
     GS, v, 350  
     N, v, 356, 461  
     grey, v, 314  
 patent blue B, v, 594  
     band 4 B, v, 282  
 pink, v, 297, 304  
 red, v, 186  
     L, v, 170  
 solid green BB, v, 242  
 victoria blue A, v, 280  
     R, v, 284  
     green, v, 241, 274, 278  
 yellow, v, 138, 146  
     L, v, 138  
 York closed oil tester, iii, 124  
 Nicholson's blue, v, 252, 270, 455  
 Nicotine, vi, 237  
     detection of, vi, 238  
     estimation of, vi, 240, 251; ix, 485  
     and piturine, distinction between, vi, 229  
     poisoning by, vi, 241  
     Schindelmeiser's reaction for, vi, 239  
     in tobacco smoke, vi, 251  
     Tóth's method for the estimation of, vi, 240  
 Iso-Nicotine, vi, 134

- Nicotinic acid, vi, 146  
*iso*-Nicotinic acid, vi, 146  
 Nigella oil, iv, 450  
 Niger oil. See *Niger seed oil*.  
 Niger seed oil, ii, 70, 151  
 Night blue, v, 255, 280, 461, 590  
     B, v, 280  
     green, v, 259, 278, 472  
     2 B, v, 280  
 Nigramine, v, 336  
 Nigraniline, v, 312  
 Nigrisine, v, 314  
 Nigrosine, v, 463, 558  
     soluble in water (Kalle), v, 326  
     water, soluble, v, 327, 467  
 Nigrosines, v, 462  
     detection of, v, 447  
 Nikkei oil, iv, 450  
 Nile blue, v, 350, 461, 467, 472, 588  
     A, v, 342, 350  
     2 B, v, 350  
     scarlet, YY, v, 552  
 Ninhydrin test for amino bases, ix, 560  
 Nirvanine, detection of, ix, 495  
 Nitranilines, vi, 62  
 Nitrates, estimation of nitrogen in the presence  
     of, i, 62  
 Nitrazine yellow, v, 582  
 Nitrazol, v, 203  
 Nitric acid, action of, on sugars, i, 296  
     colour test for oils, ii, 41  
     reaction of, with diphenylamine, vi, 96  
     test for cottonseed oil, ii, 138  
     use of, as an adulterant of lemon juice,  
         i, 564  
     oxide hæmoglobin, viii, 536  
 Nitrites, detection of, i, 241  
     test for, in bread, i, 461  
 Nitroalizarin, v, 578  
     detection of, v, 447  
 $\beta$ -nitroalizarin, v, 209  
 Nitrobenzene, iii, 211  
     commercial, iii, 214  
     detection of, in essential oil of bitter  
         almonds, iii, 424  
     small quantities of, iii, 213  
     reduction of, iii, 212  
     toxicological detection of, iii, 213  
 Nitrobenzol. See *Nitrobenzene*.  
 $\alpha$ -Nitrocamphor, iv, 208  
 Nitro-coccusic acid, v, 422  
 Nitro-colouring matters. See *Colouring matters*,  
     *nitro*.  
 Nitrocellulose, analysis of, iii, 563  
     application of Abel test to, iii, 598  
     Bergmann and Junk test for, iii, 615  
     detection of, iii, 562  
     discolouration of, iii, 568  
     estimation of, iii, 562  
         nitrogen in, iii, 563  
         unnitrated fibre in, iii, 567  
     German 135° test for, iii, 613  
     loose-fibre, application of the Abel test to,  
         iii, 605  
     microscopic examination of, iii, 569  
 Nitrocellulose powders, U. S. Army Ordnance,  
     115° test for, iii, 616  
     properties of, iii, 560  
     solubility of, iii, 565  
     solvents for, iii, 589  
     sulphuric esters in, iii, 568  
     viscosity of solutions of, iii, 569  
     Will test for, iii, 615  
 Nitro-diphenylamines, v, 128  
 Nitroethane, presence of in spirit of nitrous ether,  
     i, 243  
 Nitrogen, colloidal, in urine, ix, 575  
     in crude petroleum and paraffin oil, iii, 39  
     detection of, i, 58  
     distribution of, in wheat proteins, viii, 98  
     estimation of, by the Kjeldahl method, i, 59;  
         viii, 48  
     Arnold's modification to, i, 62  
     in nitrocellulose, iii, 563  
     organic substances, i, 58  
     the presence of nitrates, i, 62  
     protein digestion products, viii, 481  
     in malt, viii, 105  
     mode of existence of in tobacco, vi, 244  
     occurrence of in plants, vii, 238  
 Nitroglycerin, ii, 452, 472; iii, 570  
     application of the Abel test to, iii, 603  
     detection of, iii, 571  
     estimation of, iii, 572  
     examination, iii, 571  
     explosives, moisture in, iii, 592  
     stability test for, iii, 601  
 Nitronaphthalenes, iii, 260  
 Nitronaphthols, v, 125  
 2:4-Nitronaphthol-sulphonic acids, v, 127  
 Nitropentane, detection of in commercial amyl  
     nitrite, i, 252  
*o*-Nitrophenylpropionic acid, v, 456  
 Nitropinene, iv, 182  
 Nitroprussic acid, vii, 530  
 Nitroprussides, vii, 530  
 Nitrosamine red, v, 122, 124  
 Nitro-silk, viii, 638  
*iso*-Nitroso-antipyrine, vi, 40  
 Nitrosoconiine, ix, 481  

*p*-Nitroso-dimethylaniline, vi, 90  
 Nitroso-ferricyanides, vii, 530  
 $\alpha$ -Nitroso- $\beta$ -naphthol, v, 130, 131  
 Nitrosopinene, iv, 182  
 Nitroso- and *iso*-nitroso colouring matters. See  
     under *Colouring matters*.  
 Nitro-substitution compounds, detection of nitro-  
     gen in, i, 58  
 Nitrous ether, spirit of. See *Spirit of nitrous*  
     *ether*.  
     ethers, i, 241  
     saponification of, i, 241  
 Non-glucosidal bitter substances, vii, 137; ix,  
     549  
 Non-tans, value of in tanning, v, 83  
 Noodles, viii, 102  
     colouring matters in, v, 651  
 Nopalin, v, 296  
 Noratropine, ix, 490, 491  
     salts of, ix, 491

**Norhyoscyamine**, VI, 291, 298; IX, 490, 491  
 salts of, IX, 491  
**Norka**, composition of, I, 464  
**Nosophene**, III, 557  
**Novocaine**, detection of, IX, 495  
**Nucleic acid**, VIII, 70  
**Nuclein**, VIII, 436  
**Nucleoproteins**, VIII, 34, 70, 73, 92  
**Nucleosides**, VIII, 72  
**Nucleotides**, VIII, 72  
**Nut chocolate**, VI, 695, 705  
 oil. See *Walnut oil*.  
**Nutmeg butter**, II, 71, 182  
 oil, IV, 249, 357, 450  
**Nuts**, proteins in, VIII, 96  
**Nux vomica**, VI, 467; IX, 512  
 assay of, VI, 469; IX, 512  
 official preparations of, VI, 472; IX, 512  
 oil of, IX, 510  
**Nylander's test for sugars in urine**, I, 394

## O

**Oak creosote oil**, composition of, III, 353  
 English, reactions of, V, 49  
 extract, IX, 397  
 green, reactions of, V, 45  
**Oak-bark**, analysis, of, V, 67, 102  
 reactions of, V, 42  
 tannins, reactions of, V, 52  
 reduction equivalent of, V, 64  
**Oak-wood extract**, analysis of, V, 67; IX, 397  
 reactions of, V, 50  
**Oat starch**, I, 413, 415  
**Oatmeal and barley or wheat flour**, analysis of a  
 mixture of, I, 417  
**Oats**, I, 463  
 granulated, composition of, I, 464  
 proteins in, VIII, 107  
 rolled, composition of, I, 464  
**Ocimene**, IX, 324  
**Octacoline**, VI, 155  
**Odoriferous substances**, table of solubility of, IV,  
 460.  
**Ohio petroleum**, III, 42  
**Oil of absinthe**, IV, 428  
 of amber, IV, 21  
 of asafoetida, IV, 95, 434; IX, 317  
 of bergamot. See under *Bergamot*.  
 of bitter almonds. See under *Almonds*.  
 of cassia. See *Cassia oil*.  
 of cherry-laurel, composition of, III, 420  
 of cinnamon. See *Cinnamon oil*.  
 Chinese. See *Cassia oil*.  
 of cloves. See *Clove oil*.  
 of copaiba. See *Copaiba oil*.  
 of cubeba, IV, 249, 250, 333, 441; IX, 358  
 fusel. See *Fusel oil*.  
 of ginger-grass, IV, 304, 309; IX, 347  
 of lemon. See *Lemon oil*.  
 of myrrh, IV, 103; IX, 318  
 of pimento leaves, IV, 378  
 of rue, IX, 369  
 seeds, proteins of, VIII, 108  
 of sweet birch, III, 494

**Oil of theobroma**. See *Cacao butter*.  
 of turpentine. See *Turpentine*.  
 of wintergreen. See *Wintergreen oil*.  
**Oils**, analysis of by saponification by Koettstorfer's  
 process, II, 14  
 blown. See *Blown oils*.  
 colour tests of, IX, 122  
 determination of the refractive power with  
 Abbé's refractometer, II, 42  
 drip. See *Drip oils*.  
 drying, II, 3  
 and marine animal, distinction between,  
 II, 88  
 properties of, IX, 121  
 and semi-drying, distinction between, II,  
 88  
 effect of blowing on, II, 365  
 of temperature on the viscosity of, III, 148  
 essential. See *Essential oils*.  
 estimation of glycerol in, II, 477  
 of the saponification value of, II, 15  
 fatty. See *Fatty oils*.  
 fixed, absorption of oxygen by, II, 38  
 spectra of, II, 42  
 acids in, II, 9  
 action of, on polarised light, II, 45  
 analysis of a mixture of, II, 89  
 by saponification, II, 14, 21  
 bromine substitution value for, II, 27  
 thermal method for the determination  
 of the unsaturation of, II, 60  
 value for, II, 26  
 classification of, II, 64  
 according to their saponification values,  
 II, 18  
 coefficients of expansion of, II, 49  
 cohesion-figures of, II, 41  
 colour test of, II, 40  
 constitution of, II, 7  
 critical temperature of solution of, II, 63  
 crude, detection and estimation of free  
 fatty acids in, II, 75  
 of rosin in, II, 76  
 of soap in, II, 74  
 of mineral acids in, II, 75  
 examination of, for foreign matters, II,  
 74, 83  
 hydrocarbons in, II, 78  
 separation of fatty and rosin acids in,  
 II, 77  
 determination of the acetyl value of, II, 32  
 of acid value of, II, 9  
 of the drying properties of, by Bischof's  
 method, II, 38  
 by Livache's method, II, 36  
 of the Hehner value for, II, 20  
 of the purity of, by the insoluble bro-  
 mide test II, 28  
 of the Reichert Meissl value with  
 Wollny's modifications, II, 23  
 drying properties of, II, 35; IX, 121  
 elaidin reaction for, II, 39  
 electrical conductivity of, II, 45  
 estimation of, II, 4  
 extraction of, II, 3



- Oils, fixed, fatty acids from**, II, 19  
 and fats, distinction between various, II, 13  
 heat of combustion of, II, 45  
 identification of, II, 69, 84, 88  
 by the critical temperature of solution, II, 63  
 of the Valenta test, II, 62  
 interaction of, with sulphur chloride, II, 40  
 iodine value for, II, 29, 32  
 determination, by Wij's method, II, 31  
 melting points of, II, 51  
 modulus of expansion of, II, 50  
 nitric acid colour test for, II, 41  
 oleorefractometer values for, II, 43, 44  
 oxidation of, II, 36; IX, 121  
 ozone values for, II, 38  
 Poutet's elaidin test for, and Archbutt's modification, II, 39  
 properties of, II, 1  
 proportion of acids and glycerol obtained from, II, 12  
 purification of, II, 6  
 refractive power of, II, 42  
 Reichert value for, II, 22, 26  
 rise of temperature on the addition of sulphuric acid to, II, 58  
 saponification of, II, 10  
 separation of, from liquids in an emulsion, II, 6  
 solidification point determination by the A. O. A. C. method, II, 56  
 by Dalican's method, II, 55  
 by Finkener's method, II, 56  
 by Shukoff's method, II, 57  
 by Wolfbauer's method, II, 57  
 solidifying points of, II, 51  
 solubilities of, in various solvents, II, 61  
 specific gravity of, II, 46  
 temperature-reaction of, II, 60  
 spontaneous combustion of, II, 38  
 sulphuric acid colour test for, II, 41  
 temperature tests for, II, 58  
 titer test for, II, 56  
 Valenta test for, II, 62  
 viscosity of, II, 46  
 yields of, from different seeds and nuts, II, 4  
 gas, specifications for, IX, 255  
 hardened, IX, 122  
 detection of nickel in, IX, 124  
 hydrocarbon and fatty, separation of, II, 18  
 hydrogenation of, IX, 122  
 identification of, by specific gravity, II, 86  
 iodine values of, II, 392  
 liability of, to inflame spontaneously, II, 512  
 lubricating. See *Lubricating oils*.  
 mineral. See *Mineral oils*.  
 non-drying, II, 3  
 petroleum. See *Petroleum oils*.  
 Portuguese, IX, 133  
 saponification equivalent of, II, 16  
 semi-drying and non-drying, distinction between, II, 85  
 transformer, IX, 256
- Oils, vegetable, detection of, in the presence of mineral oils**, III, 160  
 non-drying and animal oils, distinction between, II, 85  
 wood-preserving, antiseptic tests of, IX, 276  
 value of higher phenols in, IX, 271
- Old fustic**, V, 408, 578
- Oleasterol**, II, 488
- Oleates, glyceryl**, II, 412  
 metallic, II, 410
- Olefines**, III, 3; IX, 233  
 and acetylenes, distinction between, III, 7  
 estimation of, III, 3; IX, 233  
 gaseous, estimation of, III, 4; IX, 234  
 in liquid hydrocarbons, estimation of, by Mills and Snodgrass, process, III, 4; IX, 233  
 and paraffins, separation of, III, 3  
 test for, IX, 234
- Oleic acid**, II, 402  
 action of sulphuric acid on, II, 410  
 commercial, II, 406  
 analyses of, II, 409  
 detection of hydrocarbons in, II, 407  
 of linseed oil acids in, II, 409  
 of neutral fats in, II, 395, 407  
 fixed oils in, II, 407  
 of palmitic acid in, II, 406  
 of stearic acid in, II, 406  
 detection of in castor oil, II, 162  
 effect of heating with alkali, II, 404  
 estimation of, II, 405  
 in rape oil, II, 9, 125  
 formation of elaidic acid from, II, 404  
 of sebacic acid from, II, 403  
 free, in olive oil, II, 109  
 and palmitic acid, eutectic mixtures of, II, 388  
 separation of, II, 396  
 preparation of, II, 402  
 of palmitic acid from, II, 404  
 properties of, II, 403, 404  
 series of acids, II, 371, 373, 375  
 and stearic acid, eutectic mixtures of, II, 388  
 esters, II, 412
- Oleins**, II, 7, 412
- Oleomargarine**. See *Margarine*.
- Oleorefractometer, use of**, II, 43
- Oleo-resins**, IV, 13, 74  
 composition of, IV, 80
- Olestranol**, II, 488
- Oleum**, III, 241
- Olibanoresene**, IV, 6
- Olibanum oil**, IV, 450  
 methoxyl number, IV, 242
- Olive oil**, II, 69, 106; IX, 131  
 action of bromine on, II, 115  
 of sulphuric acid on, II, 115  
 adulteration of, II, 111  
 composition of, II, 107  
 detection of adulteration of, II, 115  
 in almond oil, II, 103  
 of arachis oil in, II, 99, 117  
 of copper in, II, 111

- Olive oil, detection of cottonseed oil in, II, 117;  
IX, 132  
of fish oil in, II, 118  
of lard oil in, II, 118  
of linseed oil in, II, 118  
of maize oil in, II, 118  
of poppy oil in, II, 118  
of rape oil in, by Tortelli and Fortini's  
method, IX, 131  
of sesame oil in, II, 117, 146  
effect of adulterants on the saponification  
value of, II, 115  
of blowing on, II, 367  
of heat on, II, 108  
of the presence of olive-kernel oil on, II, 119  
of temperature on the viscosity of, III, 148  
elaidin test for, II, 116  
estimation of arachis oil in, II, 117  
of free acid in, II, 110  
examination of, II, 369  
for adulterants, II, 112  
extracted, IX, 133  
extraction of, II, 106  
fatty acids from, II, 108  
free acid in, II, 10  
furfuraldehyde test for, II, 145  
genuine, analysis of, II, 109  
free acid in, II, 109  
group, II, 64, 69, 91  
iodine value of, II, 113  
liability of, to inflame spontaneously, II, 513  
Maumené's test for, II, 115  
non-drying properties of, II, 108  
oleic acid (free) in, II, 109  
oleo-refractometer tests for, II, 116  
oxidation of, II, 111  
oxidising properties of, II, 116  
physical properties of, II, 107  
saponification value of, II, 115  
saponified, IX, 132  
specific gravity of, II, 112  
suitability of various oils for oiling wool, II,  
III  
unsaponifiable matter of, II, 117  
use of cottonseed oil to replace, II, 112  
uses of, II, 107  
effect of the presence of acid on, II, 110  
varieties of, II, 106, 107  
viscosity, increase of, on heating, II, 111
- Olive-kernel oil, II, 118  
comparison of, with bagasses oil, II, 119  
effect of, on olive oil, II, 119
- Onion oil, IV, 451
- Onocerol, II, 488
- Onuphin, VIII, 92
- Opal blue, V, 251, 252, 274
- Opionin, VI, 411
- Opiopon, IX, 502
- Opium, VI, 407  
action of solvents on, VI, 414  
adulteration of, VI, 416; IX, 504  
alkaloids, VI, 353, 408; IX, 496, 504  
colour reactions of, VI, 365, 366; IX, 497  
constitution of, VI, 355; IX, 496  
estimation of, VI, 370
- Opium alkaloids, formation of, IX, 477  
general characters of, VI, 361  
separation of, VI, 370  
solubility of, in various solvents, VI, 362;  
IX, 496  
assay of, VI, 416  
by the British Pharmacopoeia process, VI,  
423  
by the German Pharmacopoeia process, VI,  
427  
by the United States Pharmacopoeia proc-  
ess, VI, 419  
camphorated tincture, VI, 429; IX, 507  
composition of, VI, 408  
detection of, in cases of poisoning, VI, 435  
estimation of codeine and narcotine in, VI,  
393  
morphine in, VI, 417; IX, 504, 506  
extract of, VI, 429  
normal, IX, 506  
preparation of meconic acid in, VI, 411  
smoke, VI, 433; IX, 508  
tincture of, VI, 429  
toxicology of, VI, 434; IX, 508
- Opium-poppy, alkaloids in, VI, 353; IX, 477
- Opon, IX, 502
- Oporesinotannol, IV, 4
- Orange I, V, 139, 142, 459; IX, 453  
separation of, from the other coal-tar col-  
ours in meat products, VIII, 383
- II, V, 139, 142, 146, 459, 576  
No. 3, V, 143  
III, V, 576  
IV, V, 138, 576  
acridine. See under *Acridine*.  
alizarin. See under *Alizarin*.  
alkali. See under *Alkali*.  
aniline, V, 363  
atlas, V, 139  
B, V, 139  
brilliant, V, 139  
Chicago, V, 158  
cloth, V, 180, 580  
congo. See under *Congo*.  
crocein, V, 136, 137, 139, 142, 578  
diphenylamine, V, 138, 145  
eosin, V, 295  
ethyl, V, 458  
extra, V, 139  
G, V, 139, 142, 459, 580  
cotton, V, 158  
oxy-diamine, V, 584  
GG, V, 139  
GRx, V, 139  
GS, V, 138  
GT, V, 140, 580  
gold, V, 139, 145  
immedial, V, 376  
indanthrene. See under *Indanthrene*.  
juice, I, 560  
permesin, V, 140  
M, V, 138  
MN, V, 138, 145  
meat, composition of, I, 464  
methyl. See *Methyl orange*.

- Orange, mikado. See under *Mikado*.  
 milling. See under *Milling*.  
 N, v, 141, 146  
 $\beta$ -naphthol, v, 139, 459  
 O, pyrogene, v, 618  
 oils, iv, 359, 451; ix, 368  
   bitter, iv, 360.  
   distilled, iv, 361  
   mandarin, iv, 362, 451  
   South American, iv, 364  
   weet, iv, 359; ix, 368  
   tangerine, iv, 362, 451  
 pluto. See under *Pluto*.  
 Poirrier's, v, 137, 138  
 primuline, v, 578  
 pyramine. See under *Pyramine*.  
 R, v, 139, 580  
   alcole, v, 535, 556, 584  
   chlorophenine, v, 582  
   cibanone, v, 535  
   helindone, v, 535  
   tannin, v, 550  
 RV, v, 140  
 RR, diphenyl, v, 139  
 2 R, No. 3, v, 140  
 4 R, stilbene, v, 584  
 red I, v, 152  
 sulphonated azo-dyes, v, 137, 141  
 T, v, 139  
 thioxine. See under *Thioxine*.  
 tolylene. See under *Orange*.  
 W, v, 138  
 yellow, v, 139  
 Orange-flower oil, iv, 366, 451  
   water, iv, 368  
 Orcein, v, 427, 467  
 Orcellin deep red, v, 152  
 Orchil, v, 427, 550, 635  
   examination of, v, 428  
   red, v, 546  
   A, v, 170  
   G, v, 548  
   substitute, V, 3VN, v, 546  
 Orcin. See *Orcinol*.  
 Orcinol, III, 337, 426  
   test for pentoses, I, 401  
 Oregon balsam, iv, 79  
 Orellin, v, 421  
 Orexin, vi, 161  
   tannate, vi, 161  
 Oriental storax, III, 462  
 Origanum oil, iv, 451  
 Oriol, v, 578  
   yellow, v, 140, 143  
 Oriziba jalap, VII, 131  
 Orris oils, iv, 451  
 Orsellin BB, v, 170, 540  
   2 B, v, 161, 162  
 Orsellinic acid, III, 513  
 Orthine, vi, 32  
 Orthoform, III, 502  
 Osazones, vi, 35  
 Ossein, VIII, 585  
 Otto of roses, iv, 382, 388; ix, 373  
   congealing point of, iv, 385  
 Otto of roses, separation of citronellol and  
   geraniol in, ix, 329  
 Ouabain, VII, 123  
 Oulman's method for the estimation of potassium  
   hydrogen tartrate in argol, I, 545  
 Ovalbumin, VIII, 433  
 Ovens, constant temperature, I, 69  
   vacuum, drying, I, 69  
 Ovomucin, VIII, 433  
 Oxalates, I, 528, 531  
   estimation of, in cyanide solutions, VII, 493  
 Oxalic acid, I, 527  
   and citric acid, separation of, I, 556  
   and malic acid, separation of, I, 534  
   colour reactions of, I, 487  
   commercial, I, 530  
   detection of, in vinegar, I, 503  
   estimation of, I, 529  
   in cocoa and chocolate, ix, 97  
   formation of formic acid from, I, 528  
   in tartaric acid liquors, I, 541  
   in urine, ix, 574  
   poisoning by, I, 530  
   production of, I, 527  
   reactions of, I, 528  
 Oxaluria, ix, 574  
 Oxaluric acid, VII, 362  
 Oxamine black N, v, 564  
   blue G, v, 598  
   3 R, v, 196  
   brown 3 G, v, 616  
   fast red F, v, 556  
   green G, v, 572  
   pure blue 6 B, v, 596  
   red 3 B, v, 552  
   violet, v, 186, 608  
 Oxazines, v, 340  
   constitution of, v, 313  
 Oxazones, v, 343  
 Oxidised oils. See *Blown oils*.  
 Oxolin, iv, 152  
 Oxonitin, ix, 487  
 Oxtallow, examination of, II, 369  
 Oxyacanthine, vi, 561  
   salts of, vi, 563  
 Oxycellulose, I, 431  
   cupric reducing power of, I, 433  
 Oxycholesterol, digitonide of, ix, 547  
 Oxycholine. See *Betaine*.  
 Oxochrome black F, v, 562  
   blue B, v, 596  
   brown V, v, 616  
   garnet B, v, 552  
   violet R, v, 608  
 Oxydase, VIII, 12  
 Oxydases, VIII, 12  
   estimation of, VIII, 14  
   plant, ix, 591  
   reagents for, VIII, 13  
 Oxydiamine black NF, v, 560  
   brown 9, v, 616  
   orange G, v, 584  
 Oxydiaminogene OT, v, 566  
 Oxygen, detection and estimation of, in organic  
   substances, I, 64

- Oxyhæmoglobin**, VIII, 504, 505  
     estimation of, VIII, 560  
     hydrolysis of, VIII, 544  
     molecular weight of, VIII, 507  
     optical properties of, VIII, 512  
     preparation of, VIII, 507  
     reduction of, VIII, 527  
     specific conductivity of, VIII, 511  
     spectrum of, VIII, 512, 529  
**Oxymethylene camphor**, IV, 206  
**Oxynarcotine**, VI, 354, 361, 364, 402  
**Oxyphenine**, V, 372, 582  
     gold, V, 372  
**Oxyproteic acid**, VII, 407  
**6-Oxypurine**. See *Hypoxanthine*.  
**Oxyquinaseptol**, III, 403  
**Oxysparteine**, VI, 234  
**Ozokerite**, III, 54  
     crude, assay of, III, 56  
     purified, III, 55, 57  
     vaseline, III, 57
- P**
- Pacific blue**, V, 282  
**Padang benzoin**, III, 450  
**Paint**, extraction of linseed oil from, II, 328  
**Painters' terebene**, IV, 427  
**Palambang benzoin**, III, 450  
**Palm oil**, II, 71, 182  
     analysis of varieties of, II, 185, 186  
     as a colouring matter for butter substitutes,  
         II, 183, 310  
     commercial, II, 184  
     composition of, II, 183  
     detection of in butter, II, 310  
     mixed fatty acids from, II, 184  
     proportion of palmitic acid in, II, 185  
**Palm olein**, II, 185  
**Palatine**, V, 150  
     chrome black 6 B, V, 562  
         blue B, V, 602  
         brown W, V, 616  
         claret, V, 554  
         red B, V, 554  
     red, V, 152, 546  
     scarlet, V, 546  
**Palmarosa oil**, IV, 304, 309, 452; IX, 347  
**Palmatine**, VI, 576  
**Palmatisine**, VI, 255, 279  
**Palmetto**, V, 39  
**Palmitates and stearates**, distinction between, II,  
     399  
     glyceryl, II, 397  
     metallic, II, 397  
**Palmitic acid**, II, 395  
     and oleic acid, eutectic mixtures of, II, 388  
     and other acids, melting and solidifying  
     points of mixtures of, II, 385, 386  
     and stearic acid, distinctions between, II,  
         399  
     solidifying points of mixtures of, II, 385,  
         386, 387  
     detection of, in commercial oleic acid, II,  
         406  
**Palmitic acid**, detection of, in spermaceti, II, 276  
     preparation of, from oleic acid, II, 404  
     proportion of, in palm oil, II, 185  
     separation of, in mixtures, II, 396  
     solubility of, in alcohol, II, 396  
     esters, II, 397  
**Palmitins**, II, 397  
**Palm-kernel oil**. See *Palm-nut oil*.  
     detection of, in butter by Hinks' test, II, 301  
**Palm-nut oil**, II, 72, 195  
     composition of, II, 195  
     detection of, in tallow, II, 213  
     ethyl ester value for, II, 190  
     mixed fatty acids from, II, 72, 196  
     use of, as an adulterant for coconut oil, II,  
         189  
     stearine, II, 196  
**Panaxresenes**, IV, 6  
**Panaxresinotannol**, IV, 4  
**Pancreatin**, VIII, 492  
**Pand**, PS, V, 348  
**Panopepton**, IX, 614  
**Pantopon**, IX, 502  
**Papain**, VIII, 492, 495  
**Papaverine**, VI, 354, 363, 365, 403  
     constitution of, VI, 359  
**Papaverosine**, VI, 403  
**Papaya**, alkaloid of, VII, 1  
**Paper**, bronze, I, 479  
     cheque, I, 480  
     coated, I, 479  
     detection of acid in, I, 479  
         and estimation of casein in, I, 478  
         of rosin in, I, 477  
         of starch in, I, 477  
         of iron in, I, 479  
         of sulphur in, I, 479; IX, 80  
     estimation of fibre in, I, 476  
     examination of ash from, I, 476  
         of microscopically, I, 476  
         of new fibres for, I, 484  
         of vulcanised fibre, I, 479  
     extraction and estimation of gelatin in, I, 477  
     fibres in, I, 473, 478  
     gilt, I, 479  
     impurities in, I, 478  
     manufacture of, I, 465  
     measurement of absorbency of, I, 472  
         of breaking length of, I, 469  
         of bursting strain of, I, 471; IX, 80  
         of elasticity of, I, 470  
         of ink resisting property of, I, 472  
         of machine and cross directions of, I, 469  
         of resistance to folding, I, 470  
         of sizing qualities of, I, 472  
         of strength of, I, 467  
         of tensile strain of, I, 468  
         of thickness of, I, 467; IX, 180  
         of weight of, I, 467  
     microscopic examination of fibrous constit-  
         uents of, I, 474  
     mineral constituents of, I, 476  
     particles of dirt in, I, 478  
     sizes and weights of, IX, 80  
     sizing constituents of, I, 477

- Paper, specifications of, IX, 89**  
     testing of, I, 466; IX, 80  
     tests for, IX, 88  
     tinfoil, I, 479  
     transparent spots in, I, 478  
     waterproof, I, 479  
     waxed, I, 479  
**Parabalsam, IV, 83**  
**Parabanic acid, formation of, from uric acid, VII, 362**  
**Paracasein, VIII, 126**  
     molecular weight and valency of, IX, 596  
**Paracaseinates, IX, 595**  
**Paracholesterol, II, 485**  
**Paracoto oil, IV, 452**  
**Paracyanogen, VII, 459**  
**Paradiazine black B, v, 568**  
**Paradise oil, grains of, IV, 444**  
**Paraffin, III, 188**  
     candles, detection of stearic acid in, III, 191  
     and ceresin, separation of, IX, 257  
     in crude anthracene, action of chromic acid on, III, 280  
     detection and estimation of, III, 281  
     detection of, in spermaceti, II, 277  
     estimation of, in asphaltum, III, 82; IX, 244  
     in beeswax, II, 258  
     in colophony in, IV, 29  
     in mineral oils, IX, 257  
     in petroleum residues, III, 82; IX, 244  
     melting point of mixtures of, III, 190  
     and specific gravity, relation between, III, 188, 189  
     occurrence of  $\alpha$  and  $\beta$  methylnaphthalenes in, III, 251  
     oxidation of, III, 191  
     scale, III, 192  
     assay of, III, 192  
     determination of the melting point of, III, 194  
     solidifying point of, III, 195  
     estimation of oil in, III, 192  
     of water in, III, 193  
     Redwood's machine for testing, III, 194  
     solid, III, 18, 188  
     specific gravity of, III, 188  
     and stearic acid, melting point of mixtures of, III, 190  
     stock, estimation of true paraffin in, III, 196  
**Paraffin-wax, III, 189**  
     detection of in rose oil, IV, 385  
     estimation of in tallow, II, 213  
     indentification of, IX, 238  
**Paraffins, III, 1; IX, 238**  
     and acetylenes, distinction between, III, 7  
     separation of, III, 3  
     action of chlorine on, III, 2, 3  
     of nitric acid on, III, 2; IX, 238  
     in crude anthracene, III, 271  
     detection of, III, 3  
     estimation of, III, 3; IX, 238  
     normal, physical constants of, III, 2  
     and olefines, separation of, III, 3  
     properties of, III, 2  
**Paraform, I, 256**  
**Parafuchsin, v, 282**  
**Paragreen G, v, 576**  
**Paraguay tea, VI, 641**  
**Parahistone, VIII, 92**  
**Paralactic acid, VII, 449**  
**Paraldehyde, I, 267**  
**Para-magenta, v, 282**  
**Para-menispermine, VII, 164**  
**Paramine blue, B, v, 594**  
     blue-black S, v, 562  
     brown, v, 616  
     indigo blue, v, 594  
     navy blue 2 R, v, 594  
**Paramyosinogen, VIII, 92, 279**  
**Paranitraniline red, v, 154**  
**Paraphenylene blue, v, 461, 590**  
     blue R, v, 336  
     violet, v, 336, 461  
**Pararosaniline, v, 234**  
     blue, v, 250  
**Pararosolic acid, v, 233, 270**  
**Parasulphurin S, v, 178**  
**Paraxanthine, VII, 322, 332**  
**Paregoric, assay of, VI, 429**  
**Parillin, VII, 128**  
**Paris green, v, 259, 280**  
     violet, v, 256, 280  
     6 B, v, 272  
**Parker water absorption test of leather, v, 110**  
**Parker-Payne method for the estimation of tannins, v, 89**  
**Parme R, v, 344**  
     (paste), v, 350  
**Parsley oil, IV, 368, 452**  
**Parvoline, VI, 129**  
**Pastinac oil, IV, 452**  
**Pastry, colouring matters in, v, 651**  
**Patchoulene, IV, 186, 253, 287**  
**Patchouli oil, IV, 452**  
**Patchouli camphor, IX, 343**  
**Patchoulol, IV, 287**  
**Patent blue, v, 241, 243, 462, 590**  
     A, v, 244, 282  
     N extra, superfine, v, 282  
     V, v, 243, 282  
     fast red, v, 540  
     fustin, v, 463, 580  
     phosphine, v, 363  
**Pavy's ammoniacal cupric solution, I, 331**  
     action of maltose on, I, 363  
     use of, in the examination of urine, I, 396, 397  
**Peach-kernel oil, II, 69, 105; III, 422; IX, 130**  
     Bieber's test for, II, 104  
     detection of, in almond oil, II, 103  
     Kreis' phloroglucinol test for, II, 104  
     nitric acid test for, II, 104  
**Peachwood, v, 431, 610**  
**Peanut oil. See *Arachis oil*.**  
**Pea starch, I, 412**  
**Pebble copal IV, 52**  
**Pectin, action of acids on solutions of, I, 439**  
**Pectocelluloses, I, 434**  
**Pectose, I, 434**  
     yeast, I, 209  
**Pectoses, detection of, in cream, VIII, 194**

- Peganum harmala**, alkaloids of, VII, 35  
**Pegu brown G**, v, 618  
**Pelican blue**, v, 327  
**Pelletierine**, VI, 230; VII, 49.  
     sulphate, VII, 49  
     tannate, VII, 50  
**iso-Pelletierine**, VII, 50, 231  
**pseudo-Pelletierine**, VI, 231; VII, 50  
**Pelouze's method** for the extraction of gallotannic acid, v, 2  
**Penang benzoin**, III, 450  
**Pennyroyal oils**, IV, 377, 452  
**Pensky-Martens tester** for lubricating oils, III, 167; IX, 252  
**Pentacoline**, VI, 155  
**Pentamethylene diamine**, VII, 348  
**Pentane**, III, 111  
     preparation of, III, 112  
     testing of, III, 112  
**Pentines**, IV, 163  
**Pentosans**, I, 400  
     in cocoa, VI, 697  
     estimation of, with phloroglucinol, I, 401  
**Pentoses**, I, 400; IX, 62  
     detection of dextrose in the presence of, I, 373  
     in urine, I, 400  
     estimation of, with phloroglucinol, I, 401  
     in plant extracts, IX, 66  
     in urine, I, 400  
     methyl. See *Methyl pentoses*.  
     and methylpentoses, estimation of a mixture of, I, 403  
**Penzoldt's indigo test** for acetone, VII, 402  
**Peonine**, v, 261, 262, 274  
**Pepper**, adulteration of, VII, 58, 65  
     alkaloids, VII, 54  
     analysis of, VII, 60  
     black, VII, 59  
     cayenne, VII, 57  
     commercial, VII, 56  
     constituents of, VII, 58  
     estimation of crude fibre in, VII, 60  
     of piperine in, VII, 61  
     of starch in, VII, 61  
     long, VII, 65  
     microscopical examination of, VII, 59, 67  
     oil, IV, 452  
     starch, I, 413  
     white, VII, 59  
**Peppermint oil**, IV, 249, 250, 369, 453; IX, 370  
     adulteration of, IV, 372  
     colour test for, IV, 375  
     estimation of menthol in, IV, 229  
     French, IX, 371  
     Japanese, IX, 370, 372  
     table of the characters of varieties of, IV, 373  
     spirit of, IV, 375  
**Pepsin**, VIII, 9, 11, 491  
     estimation of the proteoclastic power of, VIII, 492  
**Pepto-mangan "Gude,"** IX, 614  
**Peptones**, VIII, 35, 476  
     commercial, VIII, 396  
     analysis of, VIII, 401  
     estimation of, in meat extracts, VIII, 408  
**Peptonised milk**. See under *Milk*.  
**Peptonoids**, liquid, IX, 614  
**Peri wool blue B**, v, 598  
**Perkin's base**, VI, 66  
     purple, v, 324  
     violet, v, 454, 604  
**Pernambuco wood**, v, 431  
**Peroxydase**, VIII, 12  
**Persea oil**, IV, 453  
**Persian berries**, v, 408, 578, 634, 637  
     yellow, v, 140, 143  
**Perthiocyanogen**, VII, 546  
**Perugen**, III, 458  
**Peruol**, III, 416  
**Peruresinotannol**, IV, 4  
**Peruscabin**, III, 416  
**Peruvian balsam**, III, 455; IX, 295  
     adulterations of, III, 457; IX, 296  
     analysis of, III, 456; IX, 295  
     balsam, tolu, and storax, distinctions between, III, 454  
**Petitgrain oil**, IV, 244, 365, 453; IX, 369  
**Petrolatum**, III, 186  
     liquidum, III, 187  
**Petrolene**, III, 59  
**Petroleum**, III, 38, 116  
     bensin, purified, III, 114  
     Californian, III, 41  
     Canadian, III, 41  
     Caucasian, III, 42  
     products of, distillation of, III, 45, 47  
     coefficient of expansion of, III, 39  
     composition of, III, 39  
     crude, assay of, III, 47  
     estimation of asphaltic matters in, III, 54; IX, 231  
     of water in, IX, 249  
     of sulphur in, III, 51  
     extraction of solid paraffin from, III, 51  
     flashing point of, III, 51  
     definition of the term, by the Petroleum Act of 1871, III, 121  
     density of, III, 38  
     detection of, in tars by the dimethyl sulphate test, IX, 278  
     determination of the calorific value of, III, 51  
     distillation of, III, 44  
     products, III, 106, 111  
     action of bromine on, III, 109, 110  
     estimation of solid paraffin in, IX, 231  
     and shale distillation products, comparison of, III, 106  
**Fuller's earth test** for, III, 48  
**Galician**, III, 43, 50  
**Hanoverian**, III, 44  
     heavy, determination of specific gravity of, IX, 247  
     naphtha, estimation of, in turpentine oil, IV, 414  
     nitrogen in, III, 39  
     occurrence of, III, 38  
**Ohio**, III, 42  
     oils, calorific value of, III, 140  
     estimation of sulphur in, IX, 248  
     relation between specific gravity and calorific power of, III, 140

- Petroleum, optical activity of, III, 44, 135  
 origin of, III, 37, 44  
 Pennsylvania, III, 40  
   natural gas from, III, 41  
 pentane from, III, 111  
 pitch, detection of, in coal-tar distillate, IX, 277  
   estimation of asphalt content of, IX, 246,  
 residues, estimation of paraffin in, III, 82  
 residuum, III, 196  
 Russian, III, 42  
   distillation of, III, 45, 47  
 specific gravity tests, III, 50  
 spirit, III, 111, 113  
   behaviour of castor oil with, II, 163  
   detection of benzene in, III, 241  
   in turpentine oil, IV, 409  
   quantitative separation of benzenes in, III, 241  
   shale naphtha and coal-tar naphtha, comparison between, III, 116  
   water in, III, 115  
   sulphur in, III, 40  
   varieties of, III, 40  
 Pettenkofer's reaction for bile-acids, VII, 420  
 Peucedanum oil, IV, 453  
 Phaseolin, VIII, 111, 112  
 Phaseolunatin, VII, 102  
   detection of  $\alpha$ -dextrose in, I, 392  
 Phellandrene, IV, 168, 171, 177; IX, 324  
   detection of, in eucalyptus oils, IV, 338  
 o-Phenacetin, VI, 99  
 p-Phenacetin, VI, 99, 100  
   detection of acetanilide in, VI, 101  
   tests for, VI, 100  
 Phenacetin and acetanilide, distinction between, VI, 44, 100  
   estimation of, in admixture, IX, 472  
   acetanilide and methylacetanilide, distinction between, VI, 87  
   and antifebrin, distinction between, VI, 103  
   detection of, in antipyrin, VI, 44  
   of p-phenetidin in, VI, 100  
   estimation of, VI, 103  
   solubility of, in various solvents, III, 294  
 Phenacetins, VI, 99  
   o- and p- distinctions between, VI, 99  
 Phenanthrene, III, 266, 269  
   behaviour of, with bensal chloride, III, 280  
   with chromic acid, III, 278  
   compound of, with picric acid, III, 275  
   detection of, in crude arthracene, III, 282  
   effect of solvents on, III, 274  
   reactions of, with metallic chlorides, III, 277  
 Phenanthridine, VI, 165  
 Phenanthridone, VI, 165  
 Phenates, true, III, 294  
 Phenazone. See *Antipyrine*.  
 p-Phenetidin, detection of, in phenacetin, VI, 100  
 p-Phenetol carbamine, VI, 104  
 Phenetol red, V, 148  
 p-Phenetole-carbamide, VII, 302  
 Phenocarboxylic acids, behaviour of, with tetravalent titanium, IX, 272  
 Phenocollum hydrochloricum, VI, 104  
 Phenocyanine, V, 350  
   US, TC, TV, V, 352  
 Phenoflavin, V, 156  
 Phenol, aqueous, melting points of, III, 292  
   bromination of, IX, 271  
   commercial, III, 304  
   estimation of cresylic acid in, by distillation, III, 317  
   phenol in, IX, 270  
   tar oils in, III, 305  
   water in, III, 305  
   fraction acids of, III, 307  
   tests for, III, 307  
   control, Rideal-Walker, IX, 277  
   and cresylic acid, differences between, III, 316  
   detection of, III, 295  
   of cresylic acid in, III, 317  
   in naphthalene, III, 250  
   in the presence of thymol, IV, 290  
   in salicylic acid, III, 471  
   in wood-tar creosote, III, 355  
   esters, III, 294  
   estimation of, III, 300; IX, 271  
   in crude carbolic acid, IX, 270  
   in disinfecting powders, III, 309  
   naphthalene in, III, 247  
   in tar oils, IX, 270  
   ethers, III, 294  
   formation of, III, 289  
   moist, colour change in, III, 293  
   properties of, III, 291  
   reaction of, with bromine, III, 298  
   solubility of, III, 292  
   sulphonates, III, 395  
   and phenyl sulphates, distinction between, III, 400  
   sulphonic acids, III, 393  
   estimation of, III, 396  
   reactions of, III, 396  
   toxicological examination for, III, 303  
   use of, in disinfectants, III, 308, 332  
   and wood-tar creosote, distinctions between, III, 358  
 Phenol-2 : 4-disulphonic acids, III, 397  
 Phenolic disinfecting liquids, III, 331  
   analysis of, III, 332  
 Phenolphthalein, III, 547, 548; V, 263, 282  
   formation of, III, 545  
   as an indicator, II, 550  
   for alkaloids, VI, 181  
   and its salts, structure of, III, 549  
   test for blood, VIII, 525  
 Phenolphosphonic acids, III, 397  
 Phenols, III, 287; IX, 270  
   behaviour of, towards teravalent titanium, IX, 272  
   benzoates of, III, 295  
   classification of, III, 287  
   colour reactions of, with chloroform and alkali, III, 297  
   detection of, in essential oil, IV, 226  
   with Millon's reagent, III, 296  
   dihydric. See *Dihydroxybenzenes*.  
   in essential oils, IV, 254  
   estimation of, IV, 226,



- Phenols, estimation of, IX, 269  
 in creosote sheep dips, III, 321  
 in essential oils, IX, 327  
 in soap, II, 426; III, 334  
 by the use of sodamide, III, 302  
 higher, in wood-preserving oils, IX, 271  
 monohydric, III, 287  
 and alcohols of the benzyl series, distinction between, III, 288  
 and phenolic ethers in essential oils, IV, 254, 287  
 separation of, in wood-tar creosote, III, 351  
 sulphonated, III, 392  
 Phenol-*o*-sulphonic acid, III, 393, 394, 396  
 Phenol-*m*-sulphonic acid, III, 393, 395, 396  
 Phenol-*p*-sulphonic acid, III, 393, 395, 396  
 estimation of, III, 396; IX, 279  
 Phenosafranine, V, 338  
 Phenoxides, III, 293  
 Phenyl acetylsalicylate, III, 505  
 benzoate, III, 295  
 brown, V, 610  
 cinnamate, III, 439  
 hydrogen sulphate. See *Phenyl sulphuric acid*.  
 salicylate. See *Salol*.  
 violet, V, 604  
 Phenylacetamide. See *Acetanilide*.  
 $\beta$ -Phenyl-acrylic acid. See *Cinnamic acid*.  
 Phenylalanine, VII, 258  
 separation of, from the hydrolysis products of proteins, VIII, 27  
 $\beta$ -Phenylallyl alcohol, III, 439  
 Phenylamine black T, V, 564  
 Phenyl- $\alpha$ -amino-propionic acid. See *Phenylalanine*.  
 Phenylaniline, VI, 88, 95  
 Phenyl-anilinomauveine, V, 327  
 1-Phenyl-2:3-dimethylpyrazolone. See *Antipyrine*.  
 Phenylene black 4 B, V, 564  
 brown, V, 163, 166, 458  
 blue, V, 341  
 Phenylene-diamines, VI, 105, 106  
*p*-Phenylene diamine, V, 206  
 hydrochloride test for blood, VIII, 525  
 $\beta$ -Phenylethylamine as a putrefaction product, VII, 346  
 Phenylformic acid. See *Benzoic acid*, III, 404  
 Phenylhydrazides, VI, 32  
 Phenylhydrazine, VI, 30  
 detection of, VI, 33  
 estimation of, VI, 34  
 reaction of, with sugars, VI, 32  
 Phenylhydrazine-nitroprusside test for formaldehyde, influence of vanillin on, I, 260  
 Phenyl-methylketone. See *Acetophenone*.  
 1-3 Phenyl-methylpyrazolone, VI, 36  
 $\beta$ -Phenylnaphthalene, reactions of, with metallic chlorides, III, 277  
 Phenylnaphthylamine, III, 272  
 Phenylnaphthylimide, detection of, in crude anthracene, III, 282  
 Phenylnaphthylimids, III, 272  
 Phenylpyrazolones, VI, 36  
 Phenylsulphuric acid, III, 399  
 Phenyl-urethane, VI, 87; VII, 287  
 Philadelphia yellow G, V, 363  
 Phlobaphenes, V, 9, 10  
 value of, in tanning, V, 83  
 Phloroglucinol, III, 535; V, 12, 13  
 reactions of, V, 51  
 test of the purity of, I, 401  
 for formaldehyde, I, 258  
 Phloroglucinol-carboxylic acid, III, 525  
 tannins, detection of, V, 12  
 Phloxin, V, 304, 306, 450, 462, 540  
 2 B, V, 546  
 P, V, 297, 304  
 TA, V, 297, 306  
 Phosphates, estimation of, in milk sugar, VIII, 206  
 Phosphine, V, 363, 368, 457, 461, 468, 472, 578  
 II, N, P, V, 363  
 detection of, V, 445  
 Phosphomolybdic acid as a reagent for alkaloids, VI, 187  
 Phosphoproteins, VIII, 35, 74  
 and nucleoproteins, distinction between, VIII, 71  
 Phosphorus, detection of, I, 63  
 estimation of, I, 63  
 in egg-yolk, VIII, 438  
 in meat, VIII, 298  
 Phosphotungstic acid as a reagent for alkaloids, VI, 188  
 Photographic flash powders, III, 617  
 Phthalanil, III, 543  
 Phthaleins, III, 545  
 detection of, V, 445  
 of phenols, V, 298  
*o*-Phthalic acid, III, 542  
 commercial, III, 544  
 estimation of, III, 545  
 test for impurities in, III, 545  
 Phthalic acids, isomeric, difference between, III, 541  
 anhydride, III, 544  
 oxide, III, 544  
 Phthalide, III, 506  
 Phthalimide, III, 544  
 Phulwara butter, II, 71, 187  
 Phylloporphyrin, VIII, 556  
 Phylloxera, use of xanthater against, I, 240  
 Physostigma seeds, assay of, VII, 27  
 Physostigmine, VII, 24; IX, 536  
 benzoate, VII, 29  
 hydrobromide, VII, 29  
 salicylate, VII, 29  
 sulphate, VII, 28  
 Physostigmol, IX, 537  
 Physovenine, VII, 30  
 Phytosterol, II, 487  
 and cholesterol, separation of, II, 491  
 effect of exposure to air on the melting point of, II, 489  
 of feeding animals on, II, 489  
 estimation of, II, 489  
 Hesse's II, 493  
 isolation of, II, 489  
 presence of in calabar beans and peas, II, 484

- Phytosterol, separation of, from allied substances of higher melting point, II, 493  
 substances analogous to, II, 487, 488, 494  
 para-Phytosterol, II, 488  
 Phytosterolins, IX, 545  
 Phytosterols, classification of, II, 485, 486  
 Picene, III, 271  
 behaviour of, with benzol chloride, III, 280  
 Pichurim bean oil, IV, 453  
 Picolines, VI, 129, 142  
 Picolinic acid, VI, 146  
 as a reagent for alkaloids, VI, 187  
 Picolonates, amino-acid, IX, 562  
 Picrates, III, 585  
 Picric acid, III, 576; V, 122, 123, 457, 462, 576  
 adulteration of, III, 582  
 and naphthol yellow, distinction between, V, 126  
 commercial, III, 582  
 compounds of, with solid hydrocarbons, III, 274  
 detection of, III, 578, 585; V, 123  
 in beer, III, 581  
 in commercial iodoform, I, 283  
 estimation of, III, 578; V, 123  
 dinitrophenol in, III, 583  
 by means of acridine, VI, 164  
 solubility of, V, 123  
 use of, as a test for alkaloids, VI, 186  
 Picrocrocin, V, 419  
 Picrol, III, 339  
 Picrotin, VII, 160  
 Picrotoxin, VII, 161  
 Picrotoxinin, VII, 161  
 Pigment brown. See *Soudean brown*.  
 Pigments, V, 623  
 Pilocarpidine and its salts, VII, 52  
 Pilocarpine, VII, 51  
 constitution of, VII, 52  
 estimation of, VII, 53  
 salts of, VII, 51  
 iso-Pilocarpine, VII, 52  
 Pilocosine, IX, 537  
 constitution of, IX, 539  
 physiological action of, IX, 540  
 salts of, IX, 538  
 Pilocosinine, IX, 538  
 physiological action of, IX, 540  
 salts of, IX, 539  
 Pimaric acid, IV, 5, 22  
 Pimento oil, IV, 244, 249, 251, 377, 453  
 detection of, in bay oil, IV, 315  
 Pimento-leaves, oil of, IV, 378  
 Pimpinella oil, IV, 453  
 Pineapple flavor, composition of, I, 235  
 Pine-bark, analysis of, V, 102  
 Pinene, IV, 168, 179  
 constitution of, IV, 185  
 hydrochloride, IV, 181  
 constitution of, IV, 185  
 in lemon oil, IV, 356  
 nitrosochloride, IV, 182  
 Pine-needle oils, IV, 249, 378, 453; IX, 372  
 table of characters of varieties of, IV, 380  
 Pinenes, isomeric, IX, 324  
 Pine-nut oil, II, 70, 151; IX, 139  
 Piney tallow, II, 71, 187  
 Pink, aniline, V, 323  
 10 B, rosophenine, V, 552  
 Casan. See under *Casan*.  
 eosin salmon, V, 295  
 new, V, 297, 304  
 R, algole, V, 536  
 Pinoresinol, IV, 3  
 Piperazine, VI, 141; VII, 197  
 hydrates, VII, 199  
 hydrochloride, VII, 200  
 picrate, VII, 200  
 urate, VII, 200  
 Piperic acid, VII, 56  
 Piperidine, VI, 141; VII, 56  
 and pyridine, distinction between, VI, 142  
 Piperine, VII, 54  
 estimation of in pepper, VII, 61  
 Piperitone, IV, 342  
 Piperonal, III, 513, 523  
 in vanilla, III, 518  
 Piperonylic acid, III, 513  
 Pipitzahuac acid, V, 230  
 Pitayo bark, VI, 480  
 Pitch, coal-tar. See *Coal-tar pitch*.  
 land, composition of, III, 62  
 petroleum. See *Petroleum pitch*.  
 water gas, III, 23  
 Pittosporum oil, IV, 453  
 Pittsburg flux, III, 94  
 Piturine, VI, 229  
 and nicotine, identity of, IX, 482  
 Plant celluloses. See *Celluloses, plant*.  
 Plants, analysis of, I, 446, 450  
 detection of alkaloids in, VI, 171  
 berberine in, VI, 555  
 estimation of amino-compounds in, VII, 277  
 asparagine in, VII, 237  
 berberine in, VI, 556  
 moisture in, I, 445  
 total nitrogen in, I, 445  
 extracts of, estimation of carbohydrates in, IX, 64  
 partition of nitrogen in, IX, 616  
 isolation of lecithin from, VII, 283  
 proteins of, VIII, 93  
 estimation of, I, 445; VIII, 52  
 proximate analysis of, I, 445  
 Plasteins, VIII, 495  
 Plaster of Paris, detection of in bread, I, 460  
 Platinic chloride, use of as a reagent for alkaloids, VI, 196  
 Platinocyanides, VII, 533  
 Platinum, detection of in organic substances, I, 63  
 Plush, analysis of, VIII, 650  
 Pluto black FR, V, 564  
 brown, V, 616  
 orange, V, 616  
 G, V, 584  
 Podocarpic acid, IV, 5  
 Poirrier's orange I, V, 137  
 II, V, 137  
 III, V, 138

- Poirrier's soluble blue as an indicator, III, 552
- Poivrette, VII, 68
- Poke berry, V, 637
- Polarimeter, Hilger, I, 52  
     Laurent's, I, 42  
     Lippich's, I, 42, 45  
     Mitscherlich, I, 50
- Polarimeters, I, 41, 307  
     comparison of scales of various, I, 53  
     preparation of reagents for, I, 308  
     sugar solution for, I, 309  
     ring-shadow, I, 50  
     table comparing various, I, 308  
     use of, I, 45
- Polyarzo-colouring matters. See under *Colouring matters*.
- Polychromine, V, 540  
     B, V, 198
- Polygalic acid, VII, 128
- Polymethylenes, IX, 236
- Polypeptides, VIII, 17, 35, 476  
     obtained by the hydrolysis of proteins, VIII, 471
- Polysaccharides, I, 286
- Polyterpenes, IV, 105, 163, 187
- Pomegranate alkaloids, VI, 230; VII, 49  
     estimation of, VI, 231  
     bark, assay of, VII, 50  
     rind, analysis, of, V, 67  
     reactions of, V, 50
- Pomegranate-tannin, V, 7
- Pomona green, V, 259, 278
- Ponceau, acid, V, 152  
     anisidine, VI, 148  
     B, V, 170  
     4 BG, V, 136, 139  
     G, V, 150  
     2G, V, 148  
     R, V, 159, 452  
     2 R, V, 148, 452  
     3R, V, 148, 150, 161, 452; IX, 453  
         separation of from the other colouring matters in meat products, VIII, 383  
     5 R, erythrin, X, V, 168  
     6 R, V, 152, 548  
     3 RB, V, 170  
     4 RB, V, 160, 168  
     6 RB, V, 160, 170  
     RT, V, 150  
     S extra, V, 161, 162, 170  
     SS extra V, 161, 162, 168  
     xylidene, V, 451
- Poplar, glucosides of, VII, 99
- Poppy 2 G, V, 582  
     2 R, 3 R, V, 548
- Poppyseed oil, II, 70, 152; IX, 139  
     change of composition of, on exposure to air, II, 345  
     commercial, II, 152  
     detection of, in arachis oil, II, 101  
     olive oil, II, 118  
     sesame oil, II, 146  
     walnut-oil, II, 158  
     fatty acids from, II, 152
- Poppyseed oil, sesame oil in, II, 152  
     uses of, II, 152  
     varieties of, IX, 130
- Popular oil, IV, 454
- Populin, VII, 100
- Pork, canned, VIII, 337  
     composition of, VIII, 270
- Porphyroxine, VI, 403  
     in opium, VI, 410
- Porpoise oil, II, 67, 73, 230  
     constants for, II, 231  
     valeric acid from, II, 230
- Pot curare, VI, 477
- Potable spirits, I, 187  
     analyses of, I, 200  
     detection of sulphates in, I, 199  
     tannin in, I, 199  
     estimation of acids in, I, 195  
     aldehydes in, I, 197  
     esters in, I, 195  
     furfural in, I, 196  
     higher alcohols in, I, 187  
     by the Allen-Marquardt method, I, 188  
     Röse-Herzfeld method, I, 191  
     sulphuric acid method, I, 192  
     non-volatile residue, in, I, 198
- Potassium acetate, I, 506  
     commercial, I, 506  
     antimonyl oxalate, I, 554  
     tartrate, I, 553  
     crude, estimation of antimony in, I, 554  
     benzoate, III, 414  
     carbonyl-ferrocyanide, VII, 532  
     cobalticyanides, VII, 532  
     copper cyanide, VII, 498  
     cyanate, VII, 537  
     cyanide, VII, 472  
         method for the estimation of formaldehyde, I, 261  
     2 : 6- diiodo-phenol-4-sulphonate, III, 398  
     diiodoresorcinol monosulphonate. See *Picrol*.  
     dinitro- $\alpha$ -naphthol-sulphonic acid, V, 127  
     ferric tartrate, I, 553  
     ferricyanide, VII, 524  
         estimation of, VII, 528  
     ferrocyanide, VII, 503  
         estimation of, VII, 511  
     gold cyanides, VII, 499  
     hydrogen tartrate, I, 551  
         effect of some acids and salts on the solubility of, I, 551  
         estimation of in argol by Oulman's method, I, 545  
     urate, VII, 378  
     indoxyl sulphate, VII, 255  
     mercuric iodide as a reagent for alkaloids, VI, 191  
     myronate. See *Sinigrin*.  
     oleate, II, 410  
     oxalates, I, 531  
     permanganate, use of as a reagent for alkaloids, VI, 197  
     phenoxide, III, 293  
     phenyl-sulphate, III, 400  
     picrate, III, 585

- Potassium platinocyanide VII, 534  
 selenocyanide, VII, 556  
 silver cyanide, VII, 498  
 sodium tartrate, I, 552  
 tartrates, I, 551  
 thiocarbimide, VII, 547  
 thiocyanate VII, 545  
*iso*-thiocyanate, VII, 547  
 urate, VII, 379  
 xanthate, preparation of, I, 240  
 zinc cyanide, VII, 476, 497
- Potato, alkaloids of, VII, 89  
 poisoning by, VII, 93  
 starch, I, 412, 414  
 estimation of water in, I, 425
- Potatoes, estimation of starch in, I, 426
- Poultry, VIII, 426  
 cold storage of, VIII, 428  
 composition of, VIII, 270, 426
- Poutet's elaidin test for fixed oils, II, 39
- Prager alizarin yellow G, R, v, 154
- Preserves, detection of gelatin in, VIII, 593
- Primerose à l'alcohol DH, v, 304
- Primrose, v, 447  
 soluble, v, 296  
 spirit, v, 297
- Primula, v, 278
- Primuline, v, 371, 468  
 base, v, 463  
 red, v, 540  
 orange, v, 578  
 yellow, v, 578
- Printing blue, v, 327, 328  
 H, R, B, v, 327
- Prolamin of oats, VIII, 107  
 of rye, VIII, 108
- Prolamines, VIII, 34, 94
- Proline, VII, 257  
 separation of, from the hydrolysis products  
 of proteins, VIII, 25
- Proof spirit, I, 111  
 calculation of the percentage of, by weight or  
 volume, to the corresponding percentage  
 of alcohol, I, 123
- Propenyl dinitrate, III, 574  
 phenols in essential oils, IV, 290  
 colour reactions of, IV, 299
- Propionates, I, 522
- Propionic acid, I, 522  
 separation of, from its lower homologues, I,  
 522
- Propyl-acetic acid, I, 524
- iso*-Propylacetic acid, I, 524
- N*-Propylamine as a putrefaction product, VII, 352
- Protamines, VIII, 33, 92
- Protase, VIII, 290
- Protein digestion products, VIII, 467  
 estimation of amino-nitrogen in, by the  
 formaldehyde titration method, VIII,  
 488  
 by the nitrous acid process, VIII, 486  
 of nitrogen in, VIII, 481  
 examination of, VIII, 476, 481  
 nomenclature and characterisation of,  
 VIII, 471
- Protein digestion products, preparation of, VIII,  
 469, 480  
 hydrolysis, estimation of aspartic and glu-  
 tamic acids in, IX, 592  
 products of, VIII, 689  
 quantitative measurement of, VIII, 9  
 separation of diamino acids, formed by,  
 VIII, 28
- Proteins, VIII, 17  
 Adamkiewics reaction for, VIII, 40  
 Almén's reagent for, VIII, 37  
 amino-acids in, VII, 270  
 formed by the hydrolysis of, VIII, 18  
 animal, table of the chief, VIII, 90  
 barley, VIII, 103  
 Bial's modification of the orcinol reaction  
 for, VIII, 41  
 biological differentiation of, VIII, 90  
 biuret test for, VIII, 39  
 in cereals, I, 452  
 chemical constants of, VIII, 79  
 classification of, VIII, 33  
 coagulable, estimation of in the form of a  
 coagulum, VIII, 54  
 coagulation of, VIII, 54  
 temperature of, VIII, 77  
 colour reactions of, VIII, 38  
 conjugated, VIII, 34, 70  
 crystalline, preparation of, VIII, 67  
 detection of, VIII, 35  
 determination of the acid and basic func-  
 tions of, VIII, 88  
 of the Hausmann numbers of, VIII, 80  
 of the sulphur content of, VIII, 79  
 of egg, VIII, 432  
 empirical composition of, VIII, 79  
 Esbach's reagent for, VIII, 38  
 estimation of, in the absence of other nitro-  
 genous products, VIII, 48  
 by adsorption by colloids, VIII, 57  
 by the dialysed ferric hydroxide method,  
 VIII, 58  
 by the gum-mastic method, VIII, 58  
 hydrolysis products of, VIII, 80  
 nitrogen in hydrolysis products of, by  
 Van Slyke's methods, VIII, 82  
 of phosphorus in, VIII, 80  
 by precipitation, VIII, 53  
 in the presence of other nitrogenous pro-  
 ducts, VIII, 50  
 of the reactive amino groups in, VIII, 89  
 carboxylic groups in, VIII, 89  
 by Stutzer's process, VIII, 51  
 in urine, by Devoto's method, VIII, 56  
 by Esbach's method, VIII, 58  
 examination of, VIII, 59  
 extraction of, VIII, 41, 59  
 gold number of, VIII, 77  
 and gums, distinction between I, 439  
 Hedin's reagent for, VIII, 37  
 identification of individual, VIII, 75  
 of leguminous seeds, VIII, 110  
 in living muscle, VIII, 279  
 maize, VIII, 106  
 malt, VIII, 103

- Proteins of milk.** See under *Milk proteins*.  
 Millon's reagent for, VIII, 38  
 Molecular weight of, VIII, 77  
 Molisch-Udransky test for, VIII, 40  
 of oats, VIII, 107  
 of oil seeds, VIII, 108  
 optical rotation of, VIII, 77  
 physical constants of, VIII, 75  
 plant, VIII, 93  
 extraction of, VIII, 95  
 polypeptides obtained by the hydrolysis of, VIII, 471  
 reactions of, VIII, 35  
 refractive indices of solutions of, VIII, 79  
 Reichl's test for, VIII, 40  
 Rhode's test for, VIII, 40  
 of rice, VIII, 107  
 of rye, VIII, 107  
 separation of the amino-acids formed by the hydrolysis of, VIII, 21  
 by precipitation with salts, VIII, 64  
 from the solutions in various solvents, VIII, 63  
 wheat, VIII, 96
- Proteoclastic enzymes.** See under *Enzymes*.
- Proteoses,** VIII, 476  
 examination of, VIII, 482  
 of malt, VIII, 104  
 wheat, VIII, 98
- Protocatechuic acid,** III, 511  
 homologues of, III, 513  
 reactions of, V, 51
- Protogelatinose,** VIII, 598
- Protopine,** VI, 354, 364, 367, 404
- Protoveratridine,** VII, 82, 88
- Protoveratrine,** VII, 82, 87
- Prulaurasin,** VII, 102
- Prune,** V, 345, 461  
 pure, V, 344, 350
- Prussian blue,** VII, 506, 588  
 estimation of, VII, 511  
 in weighted silk, VIII, 659  
 soluble, VII, 526
- Psychotrine,** VII, 41; IX, 544  
 salts of, IX, 544
- Ptomaine poisoning,** VIII, 322
- Ptomaines,** VII, 341  
 arsenical, VII, 355  
 classification of, VII, 344  
 physiological action of, VII, 343  
 table of, VIII, 323
- Pulegol,** IV, 281
- iso-Pulegol,** formation of, from citronellal, IV, 269
- Pulegone,** IV, 211
- Pulfrich's refractometer,** I, 23  
 use of, in estimating sugars, I, 316
- Pulp, mechanical or ground wood,** IX, 86  
 sulphite. See *Sulphite pulp*.  
 wood. See *Wood-pulp*.
- Pumilio oil,** IV, 379
- Pumilone,** IX, 372
- Pumpkin seed oil,** II, 70, 141
- Punicine,** VI, 230
- Pure blue,** V, 252  
 soluble blue, V, 590
- Purine bases,** VII, 320; IX, 525  
 estimation of, VII, 325  
 in urine, VII, 328  
 identification of microchemically, IX, 525  
 isolation of, VII, 338  
 separation of, by means of cuprous salts, VII, 324  
 derivatives, VI, 579
- Purple, brilliant.** See under *Brilliant*.
- ethyl.** See under *Ethyl*.
- Hessian.** See under *Hessian*.
- Perkins,** V, 324
- regina,** V, 282, 454, 461, 606
- thiogene,** V, 380
- Purpurin,** V, 211, 218, 542  
 and alizarin, distinction between, V, 215
- Purée,** VII, 395
- Putrefaction,** VII, 342
- Putrescine,** VII, 347
- Putrine,** VII, 354
- Pyraconine,** VI, 265
- Pyraconitine,** VI, 265; IX, 487
- Pyramidol brown,** V, 196
- Pyramidone,** VI, 47  
 detection of, IX, 471  
 antipyrine in, VI, 49  
 in urine, VI, 49
- Pyramine orange,** V, 188  
 R, V, 554
- Pyrazine yellow GG,** V, 586
- Pyrazolines,** VI, 35
- Pyrazolone colouring matters.** See under *Colouring matters*.
- Pyrazolones,** VI, 35
- Pyrene,** III, 267, 269  
 behaviour of, with benzal chloride, III, 280  
 with chromic acid, III, 279  
 with metallic chlorides, III, 277  
 compound of, with picric acid, III, 275  
 effect of solvents on, III, 274  
 oil. See *Bagasses oil*.
- Pyrethrum oil,** IV, 454
- Pyridine,** VI, 129, 131  
 bases, VI, 128  
 estimation of, in creosote sheep dips, III, 318  
 preparation of, VI, 130
- carboxylic acids,** VI, 145
- commercial,** VI, 139
- derivatives,** VII, 195
- detection of,** VI, 136  
 in ammonium salts, IX, 475  
 in liquor ammonii caustici, IX, 475
- dicarboxylic acid,** VI, 146
- estimation of,** VI, 137  
 in ammonia, VI, 138  
 in presence of ammonia, IX, 475
- homologues of,** VI, 142
- hydrochloride,** V, 134
- monocarboxylic acids,** VI, 145
- picrate,** VI, 135  
 and piperidine, distinction between, VI, 142
- platinichloride,** VI, 134
- salts of,** VI, 134
- tricarboxylic acids,** VI, 147

- Pyrocatechin**, III, 340  
**Pyrodine**, VI, 32  
**Pyrogallic acid**, III, 535  
**Pyrogallol**, III, 535  
     carboxylic acid, III, 525  
     and catechol, distinction between, III, 341  
     colour reaction of, with chloroform and alkali, III, 298  
     dimethyl ether, III, 539  
     and gallic and gallotannic acids, distinctions between, III, 530  
     monacetate, III, 538  
     reactions of, V, 51  
     triacetate, III, 539  
**Pyrogene black**, V, 377  
     blues, V, 378  
     brown D, V, 380  
         4 R, V, 618  
     cutch R, V, 618  
     dark green 3 B, 3 G, V, 574  
     green B, FB, FF, 2 G, 3 G, V, 380  
     greys, V, 378  
     indigo, V, 378, 600  
     olive N, V, 376  
     orange O, V, 618  
     yellow M, V, 376  
**Pyrol black B**, V, 566  
     brown G, V, 618  
**Pyroligneous acid**, I, 491; IX, 96  
     composition of, I, 491  
     determination of the strength of, I, 492  
     percentage of acetic acid in, I, 492  
**Pyrolignite of iron**, I, 511  
**Pyronaphtha**, III, 46, 118  
**Pyrone and its dyestuffs**, V, 286  
**Pyronine**, V, 461  
     and its derivatives, V, 288  
     B, V, 289, 306, 548  
     G, V, 288, 306, 468  
**Pyrosin B**, V, 296, 304  
     J, V, 304  
**Pyrotin R PO**, V, 548  
     R, R O, V, 152  
**Pyrrole**, VI, 148  
     and indole, distinction between, IX, 476  
     blue, VI, 148  
 **$\alpha$ -Pyrrolidine-carboxylic acid**. See *Proline*.
- Q**
- Quadri-urates**, VII, 373  
     formation of, in gouty subjects, VII, 380  
**Quassia and hops**, method for distinguishing between, in beer, I, 161  
**Quebrachitannic acid**, V, 7  
**Quebracho**, V, 38; IX, 398, 400  
     adulteration of, V, 104, 398  
     decomposition products of, V, 55  
     extract, analysis of, V, 67, 102; IX, 398, 400  
     detection of, V, 44  
     mangrove in, IX, 398  
     reactions of, V, 47  
**Quercetin**, V, 412, 469  
**Quercitannic acid**, V, 7, 24  
     anhydrides of, V, 25  
     and gallotannic acid, distinctions between, V, 25  
**Quercitannin**, V, 24  
**Quercitron**, V, 408, 412, 634, 637  
     bark, V, 578  
     reactions of, V, 46  
**Quillaia sapotoxin**, VII, 127  
     glucosides of, VII, 127  
**Quillaic acid**, VII, 127  
**Quinaldine**, VI, 155  
**Quinalgen**, VI, 159  
**Quinamine**, VI, 499, 536  
     and quinine, distinction between, VI, 514  
**Quinaphthalene**, V, 456  
**Quinaseptol**, III, 403  
**Quinasolines**, VI, 160  
**Quinetum**, VI, 485  
**Quinic acid**, VI, 483  
**Quinicine**, VI, 500, 543  
     and amorphous alkaloids, distinction between, VI, 545  
**Quinidine**, VI, 500, 535  
     and quinine, distinction between, VI, 514  
     cinchonine and cinchonidine, separation of, VI, 495  
     detection of, in quinine sulphate, VI, 522  
     sulphate, VI, 535  
**Quinine**, VI, 500, 507  
     acid hydrobromid of, VI, 528  
     hydrochlorid of, VI, 528  
     ammoniated tincture of, VI, 533  
     anhydrous, IX, 516  
     carbonate, VI, 529  
     chromate, VI, 529  
     and other cinchona alkaloids, distinction between, VI, 514  
     citrate, VI, 531  
         of iron and, VI, 531  
     constitution of, VI, 502  
     detection of, VI, 510; IX, 516  
     dihydrochloride, VI, 528; IX, 517  
     estimation of, VI, 511; IX, 516  
         in cinchona bark, VI, 490, 496  
     formate, IX, 518  
     glycerophosphate, IX, 518  
     herepathite test for, VI, 513  
     hydrobromides, VI, 528  
     hydrochloride, VI, 527; IX, 517  
     and morphine, separation of, VI, 511  
     oxalate, VI, 529  
     salicylate, III, 492  
     salts of, VI, 514; IX, 517  
     separation of, from other cinchona alkaloids, IX, 516  
     specific rotation of, IX, 478  
     and strychnine, separation of, VI, 461; IX, 518  
     sulphate, VI, 515; IX, 517  
         commercial, detection of other alkaloids in, VI, 518  
         of cinchonidine in, VI, 520, 522  
         of cinchonine in, VI, 521, 525  
         of cupreine in, VI, 522  
         of quinidine in, VI, 522

- Quinine**, commercial, examination of, VI, 517  
     optical assay of, VI, 524  
     Kerner test for, VI, 520; IX, 517  
     synthetic isomers of, VI, 503  
     tannate, VI, 529  
     tartrate, VI, 530  
     thalleioquin test for, VI, 511  
     tincture of, VI, 533  
         ammoniated, VI, 533  
     valerate, VI, 529  
     wine of, VI, 533
- Quinoidine**, VI, 543
- Quinol**, III, 335, 336, 339  
     colour reaction of, with chloroform and alkali, III, 298
- Quinoline**, VI, 150  
     antiseptics and antipyretics from, VI, 156  
     blue, V, 359; VI, 153  
     colouring matters. See under *Colouring matters*.  
     commercial, VI, 154  
     estimation of, VI, 154  
     reactions of, VI, 153  
     red, V, 359, 366, 448  
     salts of, VI, 152  
     Skraup's preparation of, VI, 151  
     yellow, V, 360, 457, 468, 576; VI, 155  
         spirit soluble, V, 366  
         S (water soluble), V, 366  
         water-soluble, V, 360
- Quinolinic acid**, VI, 146
- Quinol-phthalein**, III, 546, 547
- Quinone**, III, 339
- Quinophthalone**, V, 366; VI, 155
- Quinosol**, VI, 160
- Quinovic acid**, VI, 482
- Quinovin**, VI, 482

## R

- Racemic acid**, I, 536  
     in tartaric acid liquors, I, 541  
     tartaric and mesotartaric acids, separation of, I, 550
- Radish seed oil**, II, 69, 121
- Raffinose** in yeast, I, 212
- Raffinose**, detection of, in the presence of sucrose, I, 314  
     estimation of, IX, 52, 625  
     of cane sugar in the presence of, I, 313, 569  
     hydrolysis of, I, 297
- Ragweed oil**, IV, 454
- Rangoon tar**, III, 44
- Rape oil**, II, 69, 122  
     adulteration of, II, 125, 127  
     arachidic acid in, II, 123  
     Black Sea, II, 130, 131  
     blown, II, 362  
     commercial, assay of, II, 125  
     composition of, II, 123  
     constants of, II, 69, 124  
     for varieties of crude Indian, II, 124, 126  
     and cottonseed oil, distinction between, II, 370  
     crude, properties of, II, 122

- Rape oil**, detection of, in arachis oil, II, 102  
     carmeline oil in, II, 132  
     cottonseed oil in, II, 130  
     fish oil in, II, 130  
     hedge-mustard oil in, II, 130  
     linseed oil in, II, 130  
     in olive oil by Tortelli and Fortine's method, IX, 131  
     ravirus oil in, II, 130  
     train oil in, II, 130  
     effect of blowing on, II, 367  
     extraction of, II, 122  
     fatty acids from, II, 124, 129  
     flash point of, II, 129  
     free acid in, II, 10  
     group, II, 65, 69, 120  
     Halphen's colour test with, II, 129  
     iodine value of, II, 128  
     Maumené's thermal value of, II, 128  
     oleo-refractometer value, II, 44, 124  
     oxidation test for the purity of, II, 129  
     refined, properties of, II, 120  
     saponification value of, II, 128  
     solidifying point of, II, 123  
     specific gravity of, II, 127  
     unsaponifiable matter from, II, 129  
     Valenta's acetic acid test for, II, 129  
     viscosity of, II, 128  
     effect of temperature on, III, 148, 149
- Raspberry flavor**, I, 235
- Ratanhia-tannin**, V, 7
- Ratanhy root**, analysis of, V, 67
- Rational hydrometer**, I, 9
- Ravirus oil**, II, 131  
     detection of, in rape oil, II, 130
- Raw grain**, I, 144
- Rectified spirit**. See *Spirit of wine, rectified*.
- Red, acid**. See under *Acid*.  
     acridine. See under *Acridine*.  
     algole. See under *Algole*.  
     alizarin. See under *Alizarin*.  
     alkali. See under *Alkali*.  
     aniline. See under *Aniline*.  
     anisol, V, 148, 482  
     anthracene. See under *Anthracene*.  
     apollo, V, 150  
     archil, V, 161  
     atlas, V, 152, 548  
     azobenzene, V, 161  
     B. See *Soudan II*.  
     claret, V, 540  
     erio-chrome, V, 552  
     3 B, helindone, V, 536  
     G, rhoduline, V, 336  
     thioindigo, V, 536  
     B 3, trona, V, 552  
     2 B, amido-naphthol, V, 554  
     dianol, V, 196  
     4 B, chlorantine, V, 552  
     10 B, triazol, V, 554  
     brilliant. See under *Brilliant*.  
     cabbage, detection of colouring matter from, in wines, I, 181  
     carmine, V, 422  
     clayton cloth, V, 544



- Red, cloth. See under *Cloth*.  
 cochineal. See under *Cochineal*.  
 Congo. See under *Congo*.  
 coralline. See *Coralline, red*.  
 cotton, v, 192  
 cumidine, v, 548  
 dark thiogene, v, 380  
 diamine. See under *Diamine*.  
 direct. See under *Direct*.  
 eclipse. See under *Eclipse*.  
 fast. See under *Fast*.  
 G, ciba, v, 536  
     diamond, v, 552  
 G, mars, v, 550  
 glycin, v, 186  
 imperial v, 192, 296  
 indanthrene, v, 536  
 janus, v, 174  
 lead, use of, as a colouring matter in sweets,  
     I, 358  
 Magdala. See *Magdala red*.  
 naphthalene, v, 332  
 naphthionic, v, 148  
 naphthyl, v, 334  
 naphthylene, v, 170, 548  
 neutral, v, 321, 334, 548  
 new. See under *New*.  
 nitrosamine, v, 122, 124  
 orcellin deep, v, 152  
 orchil. See under *Orchil*.  
 oxamine. See under *Oxamine*.  
 palatine. See under *Palatine*.  
 para-nitraniline, v, 154  
 patent fast, v, 540  
 phenetol, v, 148  
 primuline, v, 540  
 quinoline, v, 359, 366, 448  
 R, milling, v, 546  
 S, cardinal, v, 249  
 SB, wool, v, 556  
 salmon, v, 200  
 sorbine, v, 550  
 St. Denis, v, 198, 548  
 stilbene, v, 196, 548  
 toluylene, v, 449  
 tolylene, v, 310, 321, 334, 445, 461, 548  
 vat. See under *Vat*.  
 victoria, v, 192  
 violet, 5 R extra, v, 278  
 4 RS, v, 258, 282, 606  
 5 RS, v, 258, 282, 606  
 xylidine, v, 159, 548  
 Y, mercerine wool, v, 556  
 Red-liquor. See *Aluminium acetate*.  
 Reduced indigo. See *Indigo white*.  
 Reducing sugars. See under *Sugars*.  
 Redwoods, v, 431  
 Redwood's apparatus for testing the burning  
     quality of kerosene, III, 133  
     viscosimeter, III, 151  
 Reed method of filtration in testing tannin ma-  
     terials, v, 79  
 Refraction, I, 22  
     double, I, 41  
 Refractometer, Abbé's, I, 23  
     Immersion, of Zeiss, I, 25, 28  
     Pulfrich's, I, 23  
 Refractometers, I, 22  
 Regina purple, v, 282, 454, 461, 606  
     violet, v, 606  
 Reichert-Meissl value for fats and oils, II, 23  
 Reichert-Meissl-Polenske method for butter, II,  
     283, 294  
 Remijia barks, alkaloids in, VI, 546  
 Rennet curd, VIII, 196  
 Rennet-enzyme, VIII, 125  
     test for, VIII, 130  
 Rennin, VIII, 9, 11  
 Resalgin, VI, 45  
 Resenes, IV, 6  
 Resin acids, estimation of in creosote and cresylic  
     acid sheep dips, III, 324  
     in resinate driers, IV, 35  
     and fatty acids, separation of, II, 77, 395;  
         IV, 30, 33, 73  
     alcohols, IV, 3  
     esters, IV, 2, 33  
     oil. See *Rosin oil*.  
     soaps. See *Soaps resin*.  
 Resinate driers, IV, 33  
     analysis of, IV, 35  
     estimation of free resin driers in, IV, 35  
     tests for the value of, IV, 34, 35  
 Resinates, IV, 32  
     metallic, IV, 36  
 Resinolic acids, IV, 3, 5  
 Resinols, IV, 3  
 Resinotannols, IV, 3, 4  
 Resins, IV, I; IX, 310  
     acaroid. See *Acaroid resins*.  
     acid value of, IV, 9, 10, 12  
     analysis of, IV, 2  
     and camphors, separation of, IV, 8  
     commercial, IV, 7  
     composition of, IV, 1  
     coniferous, composition of, IV, 80  
     detection of, in vanilla essence, III, 521  
     essential oils, separation of, IV, 8  
     ester numbers of, IV, 10, 12  
     examination of, IV, 7  
     general characters of, IV, 7  
     in hops, VII, 165, 167  
         estimation of, VII, 175; IX, 554  
     in india rubber, IX, 320  
         estimation of, IV, 110, 112  
     iodine absorptions of, IV, 12  
     methoxyl values of, IV, 10, 15  
     saponification value of, IV, 10  
 Resoflavine paste, v, 586  
 Resopyrine, VI, 45  
 Resorcin. See *Resorcinol*.  
     black, v, 558  
     blue, v, 344, 346, 462, 588  
     brown, v, 163, 166  
     green. See *Dinitroresorcinol*.  
     yellow, v, 139, 142  
 Resorcinol, III, 335, 336, 337  
     colour reaction of, with chloroform and alkali,  
         III, 298  
     commercial, III, 339

- Resorcinal test for formaldehyde**, I, 259  
     influence of vanillin on, I, 260  
**Resorcinol-azo-benzene**. See *m-Dihydroxy-azo-benzene*.  
**Resorcinolphthalein**, III, 546, 547  
**Resorufin**, V, 343  
**Retene**, III, 267, 270  
     behaviour of, with chromic acid, III, 279  
     compound of, with picric acid, III, 276  
**Reticulin**, VIII, 92  
**Réuniol**, IV, 383  
**Reynold's mercuric oxide test for acetone**, VII, 402  
**Rheonine**, V, 368, 370  
     A, V, 584  
**Rheumatine**, III, 492  
**Rhigolene**, III, 111  
**Rhodamine**, V, 461, 540  
     B or O, 3 B, G, G extra, 12 GM, V, 306  
     6 G extra, V, 554  
     R acid, V, 554  
     S, V, 301, 306, 468  
**Rhodamines**, III, 547; V, 299  
**Rhodine 2 G**, V, 306  
     3 G, V, 304  
     12 GP, V, 308  
**Rhodinins**, V, 448  
**Rhodinol**, IV, 261, 383  
**Rhodium oil**, IV, 454  
**Rhoduline red G, B**, V, 336  
     violet, V, 336  
**Rhosadine**, VI, 354, 364, 405  
**Rice**, I, 463  
     flakes, composition of, I, 464  
     flour, detection of, in flour, I, 463  
     proteins of, VIII, 107  
     starch, I, 413, 416  
**Ricin**, VIII, 109, 110  
**Ricinoleic acid**, II, 160  
     crude, preparation of, from castor oil, II, 160  
     series of acids, II, 371, 374, 376  
**Rideal-Walker, phenol control**, IX, 277  
**Rimini's method for the estimation of hydrazine**, VI, 26  
     test for formaldehyde, I, 258  
**Ritsert's tests for acetanilide in vanillin**, III, 520  
**Road materials, bituminous**, III, 101  
     cementing value determination, III, 105  
     determination of bitumen in, III, 102  
     volatile substances in, III, 106  
     flash test for, III, 102  
     paraffin scale determination, III, 104  
     residual coke or fixed carbon determination, III, 104  
     specific gravity determination, III, 101  
     viscosity determination, III, 105  
**Roccelline**, V, 150  
**Rochelle salt**, I, 552  
**Rock-asphalt**, III, 60  
**Rock scarlet**, BS, V, 548  
     YS, V, 200, 548  
**Rocques' method for the estimation of acetaldehyde**, I, 266  
**Röse-Herzfeld method for the estimation of higher alcohols in potable spirits** I, 191  
**Rolled oats, composition of**, I, 464  
     wheat, composition of, I, 464  
**Roman caraway oil**. See *Cumin oil*.  
**Roofing papers for testing bitumens**, III, 98; IX, 244  
**Rosalic acid**, V, 260  
**Rosamine**, V, 289, 308  
     A, acid, V, 308  
**Rosaniline**, V, 472  
     blue, V, 251, 455, 463  
     detection of, V, 447  
     detection of, in wines, I, 181  
**Rosanilines, alkylated**, V, 256  
     sulphonated, detection of, V, 445  
**Rosanthrene violet**, 5 R, V, 610  
**Rosazin**, V, 328  
**Rosazurin B**, V, 192, 542  
     G, V, 190  
**Rose bengale**, V, 308, 450, 462, 542  
     AT, G, N, V, 297  
     B, V, 308, 542  
     3 B, V, 308  
     de benzoyl, V, 156  
     geranium oil. See *Geranium oil*.  
     J B, V, 297, 304  
     oil, IV, 244, 249, 251, 382, 454; IX, 373  
         adulteration of, IV, 386, 387; IX, 373  
         composition of, IV, 383  
         physical constants of, IV, 386  
**Rosemary oil**, IV, 249, 251, 389, 454; IX, 374  
**Rosewood oil**, IV, 454  
**Rosin, American**, IV, 22  
     common. See *Colophony*.  
     grease, IV, 46  
     hardened, IV, 36  
     oil, IV, 38  
         adulteration of, IV, 40, 45  
         composition of, IV, 39  
         detection of, IV, 41  
             in castor oil, II, 161  
             in lubricating oils, III, 160, 174  
             mineral oil in, IV, 45  
         estimation of, IV, 45  
         properties of, IV, 40  
         specific gravity of, IV, 41  
         uses of, IV, 40  
     spirit, IV, 37  
         detection of, in turpentine oil, IV, 416, 421, 422  
         distillation of, IV, 413  
**Rosindone**, V, 340  
**Rosinduline**, V, 340  
     2 B, V, 328, 340  
     G, 2 G, V, 336  
**Rosin's test for bile-pigments**, VII, 426  
**Rosocyanin**, V, 415  
**Rosolane**, V, 454  
     B, R, OT in powder, V, 336  
**Rosolic acid**, V, 282  
     use of, in the estimation of alkaloids, VI, 182  
**Rosophenine pink**, 10 B, V, 552  
**Rosophenine-geranine**, V, 552  
**Rota's analysis of colouring matters**, V, 464  
**Rouge, M**, V, 186  
**Roxamin**, V, 154, 546

Rubber. See under *India-rubber*.

Rubeosin, v, 296

Rubian, v, 430

Rubidine, v, 150; vi, 129

Rubijervine, vii, 82, 85

Rubine S, v, 249, 268

iso-Rubine, v, 278, 461

Rubramine, v, 336

Rubreserine, vii, 25

Rue oil, iv, 455; ix, 369

Rufigallic acid, iii, 527

Rufigallol, v, 222, 463

Rum, i, 203

colouring matters in, v, 655

Russian green. See *Dinitroresorcinol*.

petroleum. See *Petroleum, Russian*.

Rye, i, 463

proteins of, viii, 107

starch, i, 413, 415

## S

Sabadilla, alkaloids of, vii, 69

extraction of, vii, 73

Sabadine, vii, 71, 77

Sabadinine, vii, 71, 78

Saccharic acid, formation of, from dextrose, i, 373

Saccharification test for malt, i, 139

Saccharimetry, i, 305

Saccharin, iii, 428; ix, 288

commercial, iii, 429; ix, 288

detection of, iii, 430; ix, 288

in beer, i, 164; ix, 289

benzoic acid in, iii, 430

in beverages, iii, 431; ix, 289

in foods, iii, 431; ix, 288

in milk, iii, 433

salicylic acid in, iii, 430

sugar, glucose and starch in, iii, 429

p-sulphamino-benzoic acid in, iii, 430

estimation of, iii, 433; ix, 290

in beer, i, 164; ix, 289

in cocoa powder, iii, 436

p-sulphamino-benzoic acid in, iii, 430

in wines, i, 175

preparation of, iii, 428

reactions of, iii, 430; ix, 288

soluble, iii, 429

Saccharine solutions, specific gravity of, i, 289

Saccharometers, i, 291

Saccharomyces aquifolii Grönlund, i, 215

cerevisiae, i, 214, 219

ellipsoideus, i, 215

ilicis, i, 215

mali, i, 215

membrane faciens, i, 215

pastorianus, i, 215

pyriformis, i, 215

Saccharomycetes, i, 205

characterization of, i, 210

spore formation, i, 210

variation of, i, 214

Saccharose. See *Cane sugar*.

Sachse's mercuric solution; use of, in the estimation of dextrose, i, 337

Sadtler's method for the fractional separation of asphalt into its constituents, iii, 87, 89

Safflower, v, 433, 550

as a substitute for saffron, v, 419

oil, ii, 70, 153; ix, 139

Saffron, v, 409, 418

detection of, in butter, v, 664

oil, iv, 455

Safraniline, v, 306

Safranine, v, 323, 336, 449, 461, 541

AG, extra G, S, T, v, 323, 336

AG extra, PF, GGS, GOOO, v, 323

AGT, FF extra conc., OOF, GOO, v, 336

B, v, 338

(Kalle) RAE, v, 338

MN, v, 338

T, extra, v, 467

Safranines, v, 321

detection of, v, 445

Safranisol, v, 449

Safrole, iv, 255, 291, 292

Safrosin, v, 296, 302, 308, 462, 546

Sagaresinotannol, iv, 4

Sage oil, iv, 455

Sago, i, 416

starch, i, 413, 416

Salacetol, iii, 503

Salantol, iii, 503

Salicene yellow D, v, 586

Salicin, vii, 99

detection of, in quinine sulphate, vi, 518

Salicyl tropeine, vi, 301

Salicylaldehyde test for acetone, i, 105

Salicylamide, iii, 503

Salicylates, iii, 487; ix, 304

detection of, in milk, viii, 173

estimation of, ix, 304

See also under *Metals*.

Salicylic acid, iii, 465; ix, 299

action of bromine on, iii, 480

anhydrides of, iii, 499

commercial, iii, 470; ix, 299

cresotic acid in, iii, 472

derivatives of, and their therapeutic applications, iii, 500

detection of, iii, 475; ix, 299

in beer, ix, 301

in butter, ii, 311, 312, 313

in commercial benzoic acid, iii, 406

in cream, viii, 190

hydroxy-isophthalic acid in, iii, 467

in milk, iii, 477

in oil of wintergreen, iii, 496

of phenol in, iii, 471

in preserved tomatoes, iii, 479

in saccharin, iii, 430

in wines, iii, 471; ix, 301

effect of heat on, iii, 475

estimation of, in beer, i, 163

bio-chemically, ix, 301

in butter, ii, 311, 312, 313

colourimetrically, iii, 483; ix, 303

in cream, iii, 485; viii, 195

gravimetrically, iii, 483; ix, 303

in jams, iii, 485; ix, 302

- Salicylic acid**, estimation of, in milk, III, 485  
 in the presence of phenols, III, 484  
 tannin, III, 485; IX, 302  
 in preserved eggs, IX, 620  
 volumetrically, III, 479; IX, 301  
 in wines, I, 175; III, 483  
 homologues of, III, 505  
 melting point of, III, 467  
 occurrence of, III, 466  
 in resins, IV, 3  
 preparation of, III, 466  
 properties of, III, 466  
 reactions of, III, 475; IX, 299  
 separation of *p*-hydroxy benzoic acid from,  
 III, 471  
 from tinned tomatoes, III, 486  
 solubility of, III, 466, 468  
 test for, with ferric salts, III, 476  
 uses of, III, 468  
 aldehyde, III, 499  
 esters, III, 492; IX, 305
- Salicylide**, III, 499
- Salicyl- $\alpha$ -methyl phenylhydrazones**, III, 503
- Salicyl-sulphonic acid**, III, 502, 504
- Salicyluric acid**, III, 468; VII, 395
- Saligallol**, III, 539
- Saligenin**, VII, 100
- Salinaphthol**, III, 498
- Salinigrin**, VII, 100
- Salipyrine**, III, 491; VI, 45
- Salitannic acid**, V, 7
- Salitannol**, III, 503
- Salkowski's test for cholesterol**, II, 483
- Salkowski-Schipper test for bile pigments**, IX, 580
- Salmine**, VIII, 92  
 amino-acids formed by the hydrolysis of, VIII,  
 20
- Salmon red**, V, 200
- Salol**, III, 294, 496; IX, 305
- Salophen**, III, 503
- Saloquinine**, III, 492
- Salt**, detection of, in colouring matters, V, 476  
 estimation of, in butter, II, 308
- Salumen**, III, 488
- Salveol**, III, 332
- Samatol**, III, 332
- Sambunigrin**, VII, 102
- Sandalwood**, V, 431  
 oil, IV, 249, 251, 455; IX, 375  
 adulteration of, IV, 394  
 composition of, IV, 393; IX, 375  
 examination of, by the acetylation process,  
 IV, 394  
 varieties of, IV, 395, 396
- Sandarac**, IV, 13, 14, 57
- Sandaracolic acid**, IV, 5
- Sanderswood**, V, 550
- Sangle-Ferrière method for the detection of**  
 abrastol, III, 260
- Sangle-Ferrière-Cuniasse test for methyl alcohol**,  
 I, 89
- Sanoform**, III, 501
- Santalene**, IV, 253, 287; IX, 325
- Santalin**, V, 432
- Santalol**, IV, 286, 287; IX, 343
- Santalwood oil**. See *Sandalwood oil*.
- Santonica**, estimation of santonin in, VII, 155
- Santonin**, VII, 151  
 detection of, in urine, VII, 156  
 estimation of, in santonica, VII, 155  
 in wormseed, IX, 550  
 reactions of, VII, 154
- Santoninic acid**, VII, 153
- Sapan wood**, V, 431
- Sapocarbonyl**, III, 332
- Saponification**, cold, II, 16  
 equivalent of fats o. waxes, II, 15  
 of oils, II, 16, 17  
 of esters, I, 231  
 of fruit esters, I, 235  
 of nitrous ethers, I, 241  
 of oils and fats, II, 14, 22  
 separation of the products of, II, 18  
 theory of, IX, 118  
 of triglycerides with alkali, theory of, II, 12  
 value, II, 17
- Saponins**, VII, 124  
 detection of, in beverages, VII, 129  
 preparation of, VII, 125
- Saporubrin**, VII, 127
- Sapotoxins**, VII, 124, 127
- Saprine**, VII, 352
- Saprol**, III, 332
- Sarcine**. See *Hypoxanthine*.
- Sarcosine**, VII, 272
- Sardine oil**, II, 73, 224
- Sarsaparilla**, glucosides of, VII, 128  
 root, compounds from, IX, 548
- Sarsapic acid**, IX, 548
- Sarsasaponin**, VII, 129; IX, 548
- Sarsasopogenin**, VII, 129
- Sassafras oil**, IV, 396, 456
- Satureja oil**, IV, 456
- Sausages**, VIII, 356  
 American, VIII, 361  
 artificial colouring in, VIII, 380  
 coal tar dyes in, VIII, 381  
 detection of horse-flesh in, VIII, 377  
 English, VIII, 359  
 estimation of benzoic acid in, IX, 619  
 of starch in, VIII, 373  
 examination of, VIII, 274  
 French, VIII, 360  
 German, VIII, 357  
 horse flesh, VIII, 375  
 water content of, IX, 619
- Savin oil**, IV, 456
- Savory oil**, IV, 456
- Sawdust**, detection of, in flour, I, 462
- Saybolt's testing lamp for kerosene**, III, 132  
 viscosimeter, III, 156
- Scammel's process for the estimation of cineol**,  
 IV, 286
- Scammonin**, VII, 130
- Scammony**, VII, 134  
 glucosides of, VII, 130  
 resin, VII, 132  
 root, VII, 132

- Scammony root, Mexican, VII, 133
- Scarlet, acid. See under *Acid*.
- azine, V, 328
- B, milling, V, 556
- 3 B, V, 161
- 6 BS, dianil fast, V, 552
- brilliant. See under *Brilliant*.
- clayton cloth, V, 548
- cochineal. See under *Cochineal*.
- columbia fast, 554
- cotton. See under *Cotton*.
- crocein. See under *Crocein*.
- crystal, V, 544
- diamine. See under *Diamine*.
- diazo. See under *Diazo*.
- direct. See under *Direct*.
- double. See under *Double*.
- eosin. See under *Eosin*.
- fast. See under *Fast*.
- G, V, 150
- GG, V, 546
- GR, V, 140, 150
- GT, V, 148
- 2 G and 2 R, V, 148
- G, algole, V, 536, 552
- ciba, V, 536, 552
- helindone. See under *Helindone*.
- imperial, V, 170
- J, JJ, V, 296
- palatine, V, 546
- R, V, 140, 148, 150, 542
- 2 R, V, 148, 540
- 3 R, V, 161, 540
- 4 R, V, 150, 161
- 6 R, V, 152, 546
- rock. See under *Rock*.
- S, V, 161, 162
- Sextra, 2 S, V, 546
- thioindigo, V, 536
- titan, V, 548
- V, V, 296
- wool. See under *Wool*.
- xylidine, V, 148, 159
- YY, Nile, V, 552
- Schaefer's chromic acid test for the purity of cocaine, VI, 334
- Scheibler's reagent for alkaloids, VI, 188
- Schiff's test for cholesterol, II, 483
- Schimmel's test for citronella oils, IV, 305
- Schindelmeiser's reaction for nicotine, VI, 239
- Schizosaccharomyces mellacei, I, 216
- pombe, I, 215
- octosporus, I, 216
- Schluttig and Neumann's method for the measurement of the ink resisting property of paper, I, 472
- Schneider test for india-rubber, IV, 114
- Schöllkopf's or S acid, VI, 120
- Schultze-Tiemann method for the estimation of nitrogen in nitrocellulose, III, 564
- Schweitzer's reagent, I, 430
- Scleroproteins, VIII, 34, 581
- Scombrine, VIII, 92
- i-Scopolamine, VI, 291, 300
- L-Scopolamine. See *Hyoscine*.
- Scopoleines, VI, 291
- Scopoletin, VII, 34
- Scopolia, alkaloids in, VI, 320
- Scopoline, VI, 294
- Seal oil, II, 73, 226
- effect of blowing on, II, 367
- Sebacic acid, II, 403
- Sedanolic acid, IX, 357
- Sedanonic acid, IX, 357
- Seed-lac, V, 424
- Seeds, leguminous, proteins of, VIII, 110
- oil, proteins of, VIII, 108
- Segura balsam, IV, 82
- Seidlitz powders, I, 553
- Selenhæmoglobin, VIII, 539
- Selenocyanides, VII, 556
- Selenopyrine, VI, 47
- Selinene, IX, 325
- Semicarbazide, preparation of, IV, 235
- Semiglutin, VIII, 595
- Senega root, glucosides in, VII, 128
- Senegin, VII, 128
- Sepsine, VII, 353
- Septentrionaline, VI, 255, 277
- Sericin, VIII, 92, 634
- Serine, VII, 250
- decomposition products of, VIII, 637
- separation of, from the hydrolysis products of proteins, VIII, 27
- Serpentaria oil, IV, 456
- Serum albumin, amino-acids formed by the hydrolysis of, VIII, 20
- peptic digestion of, VIII, 475
- globulin, amino-acids formed by the hydrolysis of, VIII, 20
- Sesame oil, II, 70, 141; IX, 136
- colour tests for, II, 143
- comparison of varieties of II, 143
- composition of, II, 142
- detection of arachis oil in, II, 146
- in arachis oil, II, 101
- in butter fat by Baudouin's test, II, 301
- of cottonseed oil in, II, 146
- in olive oil, II, 117
- of poppyseed oil in, II, 146
- in poppyseed oil, II, 152
- with rape oil, II, 146
- effect of temperature on the viscosity of, III, 148
- fatty acid from, II, 142
- furfuraldehyde test for, II, 143
- German. See *Cameline oil*.
- Milliau's modification to the furfuraldehyde test for, II, 145
- oleo-refractometer value for, II, 45
- rancid, furfuraldehyde test for, II, 144
- rotation of, II, 142
- Soltsein's test for, II, 145
- Tocher's test for, II, 145
- uses of, II, 141
- Sesamol, II, 142, 143
- Sesquicam phenol, IX, 354
- Sesquiterpene alcohols in essential oils, IV, 286

- Sesquiterpenes**, IV, 163, 185; IX, 324, 325  
     detection of terpenes in the presence of, IV, 174  
     in essential oils, IV, 253, 287  
**Setocyanine**, V, 282  
**Setoglucine**, V, 284  
**Seyda's test for tannins**, V, 9  
**Shaddock oil**, IV, 456  
**Shale**, bituminous, dry distillation products, III, 13  
     naphtha, III, III, 116  
     petroleum spirit and coal-tar naphtha, comparison between, III, 116  
     oil, burning, III, 117  
     action of phenol on, III, 118  
     creosote. See *Creosote, shale-oil*.  
     crude. See *Shale tar*.  
     tar, III, 16  
     composition of, III, 16  
     distillation products, III, 106  
     action of bromine on, III, 109, 110  
     and petroleum distillation products, comparison between, III, 106  
**Shark-liver oil**, II, 73, 222  
     analysis of, II, 223  
     effect of blowing on, II, 367  
**Shark-oil**. See *Shark-liver oil*.  
**Shea butter** II, 71, 187; IX, 147  
     nut oil, IX, 148  
**Sheep dips**, analysis of, III, 332  
     creosote. See *Creosote sheep dips*.  
     cresylic acid. See *Cresylic acid sheep dips*.  
**Shellac**, IV, 67; V, 424; IX, 311  
     adulteration of, IV, 68  
     analysis of, IV, 69; IX, 312  
     bromine absorption of, IX, 312  
     composition of, IV, 67  
     detection of colophony in, IV, 69; IX, 312  
     iodine absorption of, IV, 70  
     varieties of, IV, 67  
     white or bleached, IV, 73  
**Shin oil**, camphor in, IX, 367  
**Shredded wheat**, composition of, I, 464  
**Shrewsbury-Knapp test for formaldehyde in milk**, I, 259  
**Shukoff and Schestakoff's method for the estimation of glycerol**, II, 463  
**Siam benzoin**, III, 449  
**Siaresinotannol**, IV, 4  
**Siemens and Halske process for gold extraction**, VII, 501  
**Sierra Leone copal**, IV, 52  
**Silicotungstic acid**, use of, as precipitant for alkaloïds, IX, 479  
**Silk**, VIII, 632  
     action of nitric acid on, VIII, 638  
     of solvents on, VIII, 639  
     and artificial silk, distinction between, VIII, 663  
     artificial, VIII, 661  
     classification of, VIII, 663  
     estimation of the cupric reducing power of, I, 433  
     Fehling test for, VIII, 665  
     Maschner test for, VIII, 664  
     tests for, VIII, 663  
**Silk, blue**, V, 254  
     conditioning, VIII, 634  
     distinctions of, from other fibres, VIII, 646  
     Dreaper's test for, VIII, 647  
     dyeing of, VIII, 652  
     identification of dyes on, V, 486, 511  
     estimation of, VIII, 648  
     Prussian blue in, VIII, 659  
     examination of dyes on, V, 486, 511  
     fibroin, VIII, 92, 635  
     gelatin, VIII, 92  
     Lecompte's test for, VIII, 646  
     Liebermann's test for, VIII, 647  
     microscopical characters of, VIII, 640  
     mulberry, analysis of, VIII, 633  
     raw, examination of, VIII, 640  
     scouring, VIII, 634  
     solutions, optical activity of, VIII, 640  
     tests for, VIII, 646  
     Tussah, VIII, 642  
     action of solvents on, VIII, 639  
     analysis of, VIII, 633  
     microscopical characters of, VIII, 641  
     recognition of, VIII, 652  
     weighting in, VIII, 653  
**Silkworms**, VIII, 632  
**Silver cyanate**, VII, 539  
     cyanide, VII, 476  
     detection of, in organic substances, I, 63  
     estimation of, in cyanide solutions, VII, 494  
     fulminate, III, 586  
     selenocyanide, VII, 556  
     theobromine, VI, 593  
     tree, reactions of, V, 47  
**Sinabaldi's test for abrastol**, III, 259  
**Sinalbin**, VII, 105  
**Sinapine**, VII, 105  
**Sinigrin**, VII, 104  
     estimation of, in commercial mustard, VII, 107  
**Sinker test for malt**, I, 140  
**Sinox**, IX, 614  
**Sitosterol**, II, 486; IX, 548  
     in maize oil, II, 140  
     in wheat oil, II, 148  
**p-Sitosterol**, II, 486  
**Sitosterol-d-glucoside**, IX, 545, 548  
**Size**, VIII, 620  
**Skate-liver oil**, II, 221  
     effect of blowing on, II, 367  
     as a substitute for cod-liver oil, II, 220  
**Skatole**, VII, 254  
     as a putrefaction product, VII, 352  
**Skens**, cypress sumac, reactions of, V, 48  
**Sloeline RS, BS**, V, 327  
**Sludge asphalt**, III, 94  
**Van Slyke apparatus for amino-groups**, IX, 560  
**Smilasaponin**, VII, 129  
**Snake-root oils**, IV, 397, 457  
**Snuff**, VI, 249  
**Soap**, II, 415; IX, 204  
     analysis of, II, 421, 422, 446; IX, 204  
     varieties of, II, 443, 444  
     assay of, II, 421; IX, 204  
     classification of, according to the method of production, II, 417

- Soap, commercial, II, 417  
     cresol, IX, 208  
     detection of carnaüba wax in, II, 271  
         and estimation of, in crude oils, II, 74  
     estimation of colophony in, IV, 30  
         of formaldehyde in, IX, 208  
         of free alkali in, II, 437; IX, 206  
         of glycerol in, II, 433  
         of hydrocarbons in, II, 425  
         of phenols in, II, 426; III, 334  
         of sodium chloride in, II, 432  
         of sugar in, II, 434  
         of water in, II, 423; IX, 204  
     fatty acids in, II, 430; IX, 205  
     glycerin, II, 467  
     hard, II, 417  
     household and laundry, II, 423; IX, 210  
     hydrolysis of, II, 416  
     impurities in, II, 420  
     manufacturer's, II, 423  
     medicated, II, 420, 423; IX, 208  
     peroxide, available oxygen in, IX, 208  
     powders, IX, 209  
     production of, II, 417  
     scouring, IX, 209  
     separation of fatty acids in, II, 422, 430; IX, 205  
     soft, II, 417; IX, 210  
     test of quality of, II, 444  
     toilet and fancy, II, 423, 445; IX, 210  
 Soap-lyes, estimation of glycerol in, II, 478  
 Soaps, resin, IV, 32, 33  
 Sod oil, II, 505  
     oils, examination of, II, 509  
 Soda, estimation of, in creosote sheep dips, III, 318  
 Soda-lyes, estimation of ferrocyanides in, VII, 513  
 Sodio-theobromine salicylate, III, 491; IX, 305  
 Sodium acetate, I, 506  
     alizarin-sulphonate, V, 208  
     antimony lactate, VII, 447  
     benzene-sulphinate, III, 405  
     benzoate, III, 414; IX, 285  
     calcium antimony lactate, VII, 447  
     camphor, IV, 206  
     carbonate, detection of, in milk, VIII, 174  
     chloride. *See Salt.*  
     cyanamide, VII, 557  
     cyanide, VII, 472; IX, 585  
         manufacture of, VII, 474  
     2 : 6 : di-iodophenol-4-sulphonate, III, 398  
     ethyl sulphate, I, 239  
     ferrocyanide, VII, 506  
     flame, production of, I, 43  
     formate, detection of, as a preservative in  
         food, I, 521  
     glycocholate, VII, 412  
     hydrogen urate, VII, 376, 382  
     nitroprusside, VII, 530  
     oleate, II, 411  
     phenol-*p*-sulphonate, III, 395  
     picrate, III, 585  
     quadri-urate, VII, 375  
     resinate, IV, 33  
     saccharin, III, 429  
     salicylate, III, 487; IX, 304  
     Sodium sulpho-salicylate, III, 502, 504  
         theophylline sodium acetate, VI, 596  
         triphenylpararosaniline-monosulphonate, V, 253  
         urate, normal, VII, 379  
         xanthate, I, 240  
         zinc cyanide, IX, 587  
     Sørensen's formaldehyde method for estimation  
         of amino-acid nitrogen, IX, 561  
 Soja-bean oil, II, 70, 146; IX, 137  
     in linseed oil, II, 340  
 Soja-beans, II, 147  
     proteins of, VIII, 112  
 Solangustidine, IX, 541  
     salts of, IX, 541  
 Solangustine, IX, 540, 546  
 Solanidine, VII, 92  
 Solanine, VII, 89  
     alkaloids, IX, 540  
     salts of, VII, 91  
 Solar oil, III, 118  
 Solid green. *See Dinitroresorcinol.*  
     violet, V, 348  
     yellow S, V, 144  
 Soltsein's test for sesame oil, II, 145  
 Soluble alizarin blue, V, 210  
     blue, V, 252, 284, 462, 588  
     8 B, 10 B, V, 280  
     CB, V, 327  
     XG, V, 270, 284  
     primrose, V, 296  
     regina violet, V, 284  
 Solutol, III, 332  
 Solvents, behaviour of organic substances with,  
     I, 76  
     immiscible, table showing the behaviour of  
         organic substances with, I, 83  
     use of, I, 79  
     lighter than water, apparatus for use with, I, 82  
 Somatose, IX, 614  
 Sonnenschein's reagent for alkaloids, VI, 187  
 Sophorine, VII, 15  
 Sorbine red, V, 550  
 Soudan I, V, 136, 466  
     II, V, 136, 463  
     III, V, 162, 166, 463  
     black, V, 562  
     brown, V, 136, 463  
     G. *See m-Dihydroxy-azo-benzene.*  
 Soups, analyses of, IX, 618  
 Soxhlet tube, use of, I, 77  
 Soxhlet's method for the estimation of sugars with  
     Fehling's solution, I, 320  
 Sozal, III, 395  
 Soziolol, III, 398  
 Spaghetti, VIII, 102  
 Sparteine, VI, 232; VII, 68; IX, 483  
     constitution of, VII, 69; IX, 483  
     detection of, VI, 235  
     salts of, VII, 68; IX, 483, 541  
     sulphate, VI, 233  
 Spartium alkaloids, IX, 483  
 Spartyrine, VI, 234  
 Spearmint oil, IV, 249, 251, 376, 457; IX, 372



- Specific gravity, determination of, I, 4  
 table for comparison of, and Beaumé degrees, III, 390  
 rotatory power, I, 44  
 of sugars, I, 304
- Spectrographs, I, 33
- Spectrometer, Hilger's, I, 33
- Spectrometers, I, 33
- Spectrophotometer, VIII, 566  
 Hüfner, I, 38
- Sperm oil, II, 73, 232  
 adulteration detection of, by the saponification products, II, 237  
 alcohols from, II, 233, 234  
 arctic, II, 234, 235, 236, 240  
 and arctic sperm oil, differences between, II, 241  
 effect of blowing on, II, 367  
 colour test with sulphuric acid, II, 240  
 commercial, examination of, II, 235  
 composition of, II, 233  
 constants for, II, 236  
 detection of fish and blubber oils in, II, 239  
 of mineral oil in, II, 238  
 extraction of, II, 232  
 fatty acids from, II, 235  
 flashing point of, II, 239  
 group, II, 67, 73, 232  
 Holde's test for, II, 238  
 insoluble brominated esters from, II, 239  
 iodine value for, II, 240  
 refractive power of the unsaponifiable matter in, II, 239  
 saponification of, II, 233, 237  
 specific gravity of, II, 237  
 unsaponifiable matter from, II, 234  
 viscosity of, II, 240  
 effect of temperature on, III, 148, 149
- Spermaceti, II, 73, 273  
 cetyl alcohol from, II, 274  
 palmitate in, II, 274  
 commercial, II, 275  
 composition of, II, 274  
 constants for, II, 275  
 detection of, in beeswax, II, 260  
 of palmitic acid in, II, 276  
 of paraffin in, II, 277  
 of stearic acid in, II, 276  
 of stearin in, II, 276  
 of tallow in, II, 276  
 group of waxes, II, 68, 73  
 specific gravity of, II, 274
- Spermine, VII, 202,  
 bismutho-iodide, VII, 203  
 hydrochloride, VII, 202  
 phosphate, VII, 202
- Spica's test for explosives, III, 612
- Spices, colouring matters in, V, 659  
 estimation of essential oils in, IX, 293
- Spicewood oil, IV, 457
- Spigeline, VI, 235
- Spike-lavender oil, IV, 244, 351, 447, 457
- Spirit blue, V, 251, 284, 588  
 of camphor, IV, 196  
 estimation of camphor in, IV, 200
- Spirit of chloroform, I, 280  
 estimation of chloroform in, I, 280  
 eosin, V, 297, 304, 463  
 of ether, I, 231  
 compound, I, 231  
 induline (Kalle), V, 338  
 nigrosine, V, 338  
 of nitrous ether, I, 242  
 analysis of, I, 243  
 composition of, I, 243  
 concentrated, I, 247  
 detection of aldehyde in, I, 245  
 of ethyl chloride and other chlorinated bodies in, I, 245  
 of nitrite in, I, 246  
 of nitrates in, I, 247  
 determination of ethyl nitrite in, I, 245  
 deterioration of, I, 243  
 use of methylated spirit in the preparation of, I, 246  
 primrose, V, 297  
 proof. See *Proof, spirits*.  
 violet, V, 284, 604  
 of wine, rectified, I, 111  
 yellow. See *Aniline yellow*.
- Spirit-soluble induline, V, 467
- Spirits, potable. See *Potable spirits*.
- Spongin, VIII, 92, 672
- Spongosterol, II, 486; VIII, 673
- Spoon-wort oil, IV, 457
- Sprengel's tube, determination of specific gravity of liquids by means of, I, 6
- St. Denis red, V, 198, 548
- Stahlschmidt's method for the estimation of caffeine in tea, VI, 606
- Stammer chromometer for kerosene, III, 131
- Stantienite, IV, 18
- Staphisagrine, VII, 16
- Staphis-agroïne, VII, 16
- Star-anise oil, IV, 311, 314; IX, 351
- Starch, I, 407  
 acorn, I, 413  
 action of acids on, IX, 77  
 of enzymes on, IX, 77  
 addition of, to yeast, I, 224  
 in aqueous solution, detection of, I, 419  
 arrowroot, I, 417  
 arum, I, 413  
 barley, I, 412, 415  
 estimation of, I, 423  
 bean, I, 412  
 buckwheat, I, 413  
 canna, I, 412, 413  
 cellulose, I, 408  
 commercial, I, 425  
 corpuscles, structure of, I, 408  
 dari, I, 413  
 detection of, as an adulterant of honey, I, 384  
 in coffee, VI, 672  
 in cream, VIII, 194  
 and dextrin, distinction between, I, 428  
 and erythrodextrin, distinction between  
 action of iodine on, I, 420  
 estimation of, I, 420; IX, 70  
 in cocoa, VI, 711

- Starch, estimation of, by the diastase method,  
I, 420; IX, 71  
by the hydrochloric acid method, I, 420  
in infants' foods, VIII, 233  
by Märcker and Morgen's method, I,  
423  
in paper, I, 477  
in pepper, VII, 61  
in potatoes, I, 426  
in the presence of proteins, VIII, 103  
in sausage, VIII, 373  
formation of dextrin from, I, 427  
gelatinisation temperatures of, I, 407  
and gums, distinction between, I, 439  
iodised, I, 419  
lentil, I, 412  
maize, I, 413, 416  
oat, I, 413, 415  
pea, I, 412  
pepper, I, 413  
potato, I, 412, 414, 425  
    estimation of water in, I, 425  
rice, I, 413, 416  
rye, I, 413, 475  
sago, I, 413, 416  
separation of cellulose from, I, 435  
    of dextrose from, I, 428  
solid, detection of, I, 418  
soluble, I, 407  
    preparation of, I, 136  
solution, reaction of, with iodine, I, 419  
tapioca, I, 413, 416  
wheat, I, 412, 415, 425
- Starches, analysis of a mixture of, I, 417  
cereal, I, 417  
    estimation of, IX, 76  
    polarimetric estimation of, I, 424  
classification of, by microscopical appear-  
ance, I, 411  
examination of, with polarised light, I, 410  
leguminous group of, I, 411, 412, 417  
microscopic appearance of the more impor-  
tant, I, 412, 414  
    identification of, I, 409  
potato group of, I, 411, 412  
rice group of, I, 411, 413  
sago group of, I, 411, 413  
viscosities of solutions of, I, 427  
wheat group of, I, 411, 412
- Starch-sugar, I, 377  
as an adulterant of honey, I, 384, 387  
commercial, analysis of, I, 378, 379  
    constituents of, I, 379  
    impurities in, I, 378  
    production of, I, 378  
estimation of, in brewing, IX, 10  
in sweets, I, 358  
gallisin in, I, 379  
liquid varieties of, I, 377  
preparation of lactic acid from, VII, 430  
relative proportions of dextrose, maltose and  
dextrin in, I, 380  
use of as an adulterant of cane sugar, I, 354  
varieties of, I, 377
- Stavesacre, alkaloids of, VII, 15
- Stearates, II, 399  
    glyceryl, II, 401  
    and palmitates, distinction between, II, 399
- Stearic acid, II, 398  
and other acids. Melting and solidifying  
points of mixtures of, II, 385, 386  
commercial, II, 399  
detection of, in beeswax, II, 255  
in commercial oleic acid, II, 496  
in paraffin candles, III, 191  
in spermaceti, II, 276  
estimation of, in a mixture of fatty acids, II,  
393  
and oleic acid, eutectic mixtures of, II, 388  
and palmitic acid, distinctions between, II,  
399  
    separation of, II, 396  
    solidifying point of mixtures of, II, 385, 386,  
387  
and paraffin, melting point of mixtures of, III,  
190  
series of acids, II, 371, 372, 375  
    separation of, II, 382  
    from acids of other series, II, 389  
esters, II, 401
- Stearine, II, 398, 401  
cotton oil. See *Cotton oil stearine*.  
detection of, in spermaceti, II, 276
- Stearins, II, 7
- Stearoptene in rose oil, IV, 384
- Sterilised milk. See under *Milk*.
- Stiasny test for tannins, V, 8
- Stick-lac, V, 424
- Stiecker's test for purine bases, VII, 331
- Stigmasterol, II, 487, 488, 493; IX, 548
- Stilbene, III, 440  
orange, 4 R, V, 584  
reaction of, with benzal chloride, III, 280  
metallic chlorides, III, 277  
red, V, 196, 548  
yellow 4G, V, 586
- Stillingia tallow. See *Chinese vegetable tallow*.
- Stockholm tar, III, 20
- Stock's process for the crystallisation of fat, II, 322
- Storax, American, III, 462  
liquid, III, 461  
    analysis of, III, 462; IX, 297  
    Pharmacopœia requirements for, IX, 295  
    tests for, III, 462  
oriental, III, 462  
and Peru and Tolu balsams, distinctions be-  
tween, III, 454  
resinous adulterants of, III, 465
- Storesinol, IV, 3
- Stovaine, detection of, IX, 495
- Stramonium seeds, alkaloid in, VI, 319
- Strawberry flavor, composition of, I, 235
- Straw fibres, microscopic appearance of, in paper,  
I, 475
- Strontium cyanide, VII, 475  
salicylate, III, 488  
sucrate, I, 341
- Strophanthidine, VII, 122
- Strophanthin, VII, 122; IX, 547
- pseudo-Strophanthin, VII, 123

- Strophanthus, glucosides of**, VII, 121
- Strychnia.** See *Strychnine*.
- Strychnine**, VI, 441  
 detection of, VI, 444  
 brucine in, IX, 510  
 in cases of poisoning, VI, 456  
 estimation of, in nux vomica, VI, 469  
 in strychnine preparations, VI, 461  
 in vermin-killers, VI, 463  
 and gelsemine, distinction between, VII, 33  
 official preparations of, VI, 459  
 oxidation test for, VI, 448  
 periodide, VI, 443  
 physiological test for, VI, 454  
 and quinine, separation of, VI, 461; IX, 518  
 reactions of, VI, 444  
 salts of, VI, 443  
 toxicology of, VI, 455
- Strychnine-sulphonic acid**, VI, 443
- Strychnos alkaloids**, VI, 441; IX, 510  
 estimation of, VI, 401
- Sturgeon oil**, II, 226
- Sturine**, VIII, 92
- Styracin**, III, 439
- Styrax liquidus**, IX, 298  
 præparatus, IX, 298  
 purificatus, IX, 297
- Styrone**, III, 439
- Styryl alcohol**, III, 439
- Suakim gum**, I, 441
- Subliming point of organic substances, determination of**, I, 16
- Succinic acid**, I, 531  
 commercial, I, 533  
 impurities in, I, 533  
 estimation of, in wine, IX, 97  
 and malic acid, distinction between, IX, 99  
 preparation of, by the dry distillation of amber, I, 531  
 reactions of, I, 532  
 separation of, from other organic acids, I, 532  
 test for the purity of, I, 533
- Succinite**, IV, 18
- Succinoresinol**, IV, 3
- Sucrates**, I, 340
- Sucroclasts**, VIII, 6
- Sucrol.** See *Dulcine*.
- Sucrose.** See *Cane sugar*.
- Sugar, bush bark, reactions of**, v, 47  
 cane. See *Cane sugar*.  
 confectionery, I, 358  
 of lead, I, 512  
 maple. See *Maple products*.  
 products, examination of, I, 334  
 solutions, clarifying of, I, 310  
 normal, preparation of, I, 307  
 preparation of, for use in polarimeters, I, 309  
 specific gravity of, I, 289, 292  
 table for the comparison of degrees Brix and degrees Baumé, I, 292  
 correction of the readings of the Brix spindle at various temperatures, I, 293
- Sugar-cane, composition of**, I, 359  
 juice, I, 359  
 analysis, of, I, 360
- Sugars**, I, 285; IX, 19  
 action of alkalis on, I, 298  
 dilute acids on, I, 296  
 nitric acid on, I, 296  
 organic acids on, I, 296  
 strong acids on, I, 296  
 sulphuric acid on, I, 296  
 analysis of, influence of basic lead acetate in, IX, 49  
 of mixture of, I, 304  
 in cacao beans, VI, 703  
 classification of, I, 285  
 in coffee, VI, 643  
 colour reactions of, I, 302  
 cupric reducing power of, I, 303  
 determination of, I, 305  
 detection of, in commercial benzoic acid, III, 407  
 in glycerin, II, 475  
 in saccharin, III, 429  
 estimation of, VIII, 7, 689; IX, 22, 625  
 in admixture, I, 303  
 beet, I, 360  
 biochemically, IX, 55  
 in cocoa, VI, 713  
 in condensed milk, VIII, 213  
 in cured meat, VIII, 372  
 by fermentation with yeast, I, 299  
 by means of the refractometer, I, 316  
 in pickle for meat curing, VIII, 369  
 in soap, II, 434  
 in tanning materials, v, 100  
 fermentation of, I, 298, 299  
 and glycerin, separation of, II, 476  
 and gums, distinction between, I, 439  
 hydrolysis of, I, 296  
 inversion of, I, 296  
 isolation of, I, 286  
 reaction of, with cupric salts in alkaline solution, I, 317  
 with mercury solutions, I, 337  
 with phenyl hydrazine, VI, 32  
 recognition of, I, 302  
 reducing action of, I, 317  
 calculation of the weight of copper corresponding with, I, 328  
 detection of, I, 318  
 estimation of, I, 303; IX, 24, 29  
 by Allihn's method, I, 323  
 by A. O. A. C, gravimetric method, IX, 28  
 by Bang's method, I, 335  
 by Fehling's solution gravimetrically, I, 323, 327  
 by Soxhlet's method, I, 320  
 volumetrically, I, 319  
 by the formation of cupric nitrate, I, 336  
 gravimetrically, I, 323; IX, 28  
 by Low's method, IX, 41  
 by method of Brown, Morris and Millar, IX, 24

- Sugars, reducing action of, estimation of with Pavy's ammoniacal cupric solution, I, 331  
 in the presence of sucrose, I, 328; IX, 39, 42, 625  
 with Violette's solution, I, 333  
 volumetrically, I, 333; IX, 24, 38  
 in wines, I, 170  
 influence of special conditions on, I, 336  
 precipitation of, by basic lead acetate, IX, 625  
 solution densities of, IX, 19  
 specific rotatory power of, I, 303, 305  
 starch. See under *Starch*.  
 table of group tests for, I, 301  
 weight of copper and copper oxide obtained from the principal, I, 569
- Sugar-vinegars, I, 498
- Suint. See *Wool fat*.
- Sulphæmoglobin, VIII, 538
- p*-Sulphaminobenzoic acid, detection of, in saccharin, III, 439
- 1-2-Sulphamin benzoic anhydride. See *Saccharin*.
- Sulphamine brown A, B, V, 156
- Sulphanil yellow, V, 178
- Sulphanilic acid, VI, 61
- Sulphates, estimation of, in milk sugar, VIII, 205  
 See also *Parent substances*.
- Sulphides, estimation of, in paper, I, 479
- Sulphindigotic acid, V, 388
- Sulphine A, V, 586
- Sulphite cellulose products. See *Pseudo-tannins*.  
 pulp, IX, 84  
 manufacture of, IX, 88
- Sulphites, estimation of, in food gelatin, VIII, 617
- Sulphmethæmoglobin, VIII, 538
- Sulphocarbolic acid. See *phenol-p-sulphonic acid*.
- Sulphocyanides. See *Thiocyanates*.
- Sulphocyanine black 4 B, V, 564
- Sulpholeic acid, II, 410
- Sulphon acid green B, V, 572  
 yellow 5 G, V, 586
- Sulphonated aniline blues. See *Aniline blues*, *sulphonated*.  
 azo-colouring matters. See under *Colouring matters*.
- Sulphonazurin, V, 182, 590
- Sulphonic acids, phenol, III, 393
- Sulphophenic acid. See *Phenol-p-sulphonic acid*.
- Sulphopurpuric acid, V, 387
- Sulphosalicylic acid, III, 502
- Sulphovinates. See *Ethyl sulphates*.
- Sulphur, action of linseed oil on, II, 353  
 black T extra, V, 377, 566  
 blue L extra, V, 600  
 brown G, V, 616  
 chloride, interaction of, with oils, II, 40  
 compounds in essential oils, IV, 257, 299  
 detection of, I, 63  
 estimation of, I, 63  
 in asphalts, III, 85  
 in crude petroleum, III, 51  
 in india-rubber, IV, 126  
 in kerosene, III, 134  
 in meat, VIII, 297
- Sulphur, estimation of, in proteins, VIII, 80  
 in spent gas purifying mass, VII, 522  
 in vulcanised rubber, IV, 138  
 green G extra, V, 574  
 indigo B, V, 602
- Sulphuric acid colour test for oils, II, 41  
 method for the estimation of higher alcohols in potable spirits, I, 192
- Sulphurous acid, estimation of, in disinfecting powder, III, 311  
 in food gelatin, VIII, 617  
 in wines, I, 174
- Sumac, V, 37, 49, 637  
 adulteration of, V, 102  
 analysis of, V, 67, 69, 102  
 cape, colouring principle of, V, 55  
 detection of, IX, 399  
 estimation of catechol tannins in, V, 8  
 extracts, detection of, V, 44  
 reactions of, V, 49
- Sumac-tannin, V, 7
- Sumaresinotannol, IV, 4
- Sumatra benzoin, III, 449  
 test for, IX, 294
- Sun yellow, V, 132
- Sunfish oil, II, 223
- Sunflower oil, II, 70, 154; IX, 140
- Sweet birch oil, IV, 457  
 spirit of nitre. See *Spirit of Nitrous ether*.  
 of salt. See *Ethyl chloride*.
- Sweets, I, 358  
 analysis of, I, 358  
 colouring matters in, I, 358  
 essences from, I, 358  
 estimation of sugar in, I, 358
- Sylvestrene, IV, 168, 171, 178  
 inactive, IX, 324
- Sylvic acid, IV, 22
- Syringin, VII, 99
- Syrup, assay of, I, 352  
 of the phosphates of iron, quinine and strychnine, VI, 460  
 of Tolu balsam, III, 461

## T

- Tacca arrowroot, I, 413
- Tallow, II, 72, 208  
 bassia. See under *Bassia*.  
 Borneo. See under *Borneo*.  
 Chinese vegetable. See under *Chinese*.  
 commercial, II, 209  
 detection of, in cacao butter, II, 178, 180  
 of coconut oil in, II, 213  
 of cotton seed oil and stearine in, II, 211  
 of horse fat in, II, 212  
 of lime soap in, II, 211  
 of palm nut oil in, II, 213  
 of wool grease in, II, 212  
 in spermaceti, II, 276  
 estimation of paraffin wax in, II, 213  
 free oleic acid in, II, 209  
 group of fats, II, 66, 72, 204  
 iodine value of, II, 211  
 impurities in, II, 210

- Tallow, mafura**, II, 71, 182  
 mixed fatty acids from, II, 72, 209  
 mutton, II, 208  
 oil, II, 72, 202  
   effect of temperature on the viscosity of, III, 148, 149  
 Piney, II, 71, 187  
 saponification value of, II, 211  
 stearic acid in, II, 208  
 water in, II, 210
- Talwaan**, reactions of, V, 48
- Tampico jalap**, VII, 131
- Tan**, white, IX, 399
- Tanacetone**, IV, 212
- Tangerine orange oil**, IV, 362, 451
- Tangkawang fat**. See *Borneo tallow*.
- Tan-liquors**, estimation of free acid in, V, 97  
 examination of, V, 75, 78, 96  
 fermentation in, V, 98
- Tannic acid**. See *Gallotannic acid*.  
 acids. See *Tannins*.
- Tannin**, animal. See *Animal tannin*.  
 black, V, 558  
 extracts, V, 57; IX, 395, 400  
   adulteration of, V, 104  
   solubility of, V, 82  
 heliotrope, V, 330  
 materials, V, 31; IX, 384, 395  
   American leather chemists' association  
     official method of testing, V, 76, 79; IX, 385  
   assay of, V, 55; IX, 385  
   colour valuation of, V, 95; IX, 414  
   detection of, V, 40, 44  
   estimation of sugar content of, V, 100  
   European official method of testing, V, 71, 79  
   examination of, in leather, IX, 414  
   non-tans in, IX, 400  
   preparation of reagents for, V, 53  
   reactions of, V, 40, 44  
   sampling of, V, 56, 79; IX, 386, 390  
   treatment of solutions with hide powder, V, 83; IX, 388  
   United States of America Department of Agriculture official method of testing, V, 81  
 orange R, V, 550  
 substitutes, V, 100; IX, 406  
   detection of, IX, 409  
 of tea, estimation of, V, 66, 88, 91; VI, 614; IX, 529  
   by Allen and Fletcher's process, VI, 617  
   by Eder's process, VI, 619  
   by Löwenthal's process, VI, 615
- Tannins**, V, 1; IX, 384  
 acetic acid lead acetate test for, IX, 401  
 action of dilute acids on, V, 9  
   of fused alkali on, V, 12  
   of heat on, V, 6  
   of various reagents on, V, 14  
 alcoholic and aqueous, distinction between, V, 6  
 analysis of, IX, 385  
   use of gelatin or fish glue in, IX, 606
- Tannins**, Bennet's test for, IX, 403  
 classification of, V, 3  
 constitution of, V, 3, 7; IX, 385  
 Dieterich test for, IX, 403  
 dyeing properties of, V, 54; IX, 404  
 effect of, on the activity of enzymes, VIII, 2  
 Eitner-Philip sulphide test for, IX, 404  
 estimation of, V, 55, 85; IX, 385, 404  
   in bark, V, 94  
   by Dreaper's volumetric copper process, V, 70  
   electrolytically, V, 95  
   by Gerland's process, V, 89  
   in hops, V, 91; VII, 187  
   by means of iodine, V, 92  
   by oxidation process, V, 60, 66, 68  
   by Parker-Payne process, V, 89  
   by precipitation, V, 85, 86; IX, 393  
   in wines, I, 175; V, 86, 88  
   in writing inks, IX, 468  
 extraction of, V, 2; IX, 386  
 ferric chloride test for, V, 5  
 formaldehyde test for, IX, 401  
 gold chloride test for, V, 9  
 Hoppenstedt test for, IX, 403  
 Konstein's test for, IX, 403  
 Langmann's molybdate figure for, IX, 394  
 lead acetate test for, IX, 401  
 percentage of, in tannin yielding materials, V, 31  
 phloroglucinol. See *Phloroglucinol tannins*.  
 reduction equivalents of, V, 64  
 separation of, from cider, IX, 393  
 Seyda's test for, V, 9  
 solubility test for, IX, 402  
 Stiasny tests for, V, 8; IX, 394  
 sugar content of, IX, 406  
 tests for, V, 40; IX, 394, 401, 407
- pseudo-Tannins**, IX, 406
- Tans synthetic**, IX, 409
- Tansy oils**, IV, 457
- Tapioca**, I, 416  
 starch, I, 413, 416
- Tar**, blast-furnace, III, 18  
 coke-oven. See *Coke-oven tar*.  
 gas works. See *Gas-works tar*.  
 oils, estimation of phenol in, IX, 270  
   heavy, III, 209  
 Rangoon. See *Rangoon tar*.  
 shale. See *Shale tar*.  
 water-gas, III, 34
- Tars**, III, 14  
 dimethyl sulphate test, IX, 278  
 separation of water from, III, 14
- Tartar**, I, 543  
 emetic. See *Potassium antimonyl tartrate*.  
 crude. See *Argol*.
- Tartaric acid**, I, 536  
 action of oxidising agents on, I, 537  
   with resorcinol, I, 487  
 and citric acid, separation of, I, 556  
 and malic acid, separation of, I, 535  
 British Pharmacopoeia requirements for, IX, 103

- Tartaric acid, commercial**, I, 539  
 lead in, IX, 101  
 tests for, IX, 101  
 detection of, I, 537  
 in citric acid, IX, 115  
 in vinegar, I, 49, 503  
 estimation of, I, 537, 539; IX, 103  
 by Beis' method, IX, 105  
 detection of petroleum and asphalt in, by  
 by Chapman and Whitteridge's method,  
 IX, 104  
 by Goldenburg method, IX, 103  
 by Kling's method, IX, 105  
 in cream of tartar, IX, 103  
 in presence of malic and succinic acids,  
 IX, 106  
 in tartaric acid liquors, I, 540  
 in wine, IX, 13, 109  
 lead in, I, 568  
 forms of, I, 536  
 in commercial citric acid, I, 558  
 in wine, I, 539
- L-Tartaric acid**, I, 536  
 liquors, I, 540  
 assay of, I, 549  
 manufacture of, IX, 99, 101  
 mesotartaric and racemic acids, separation  
 of, I, 550  
 specific gravity of aqueous solutions of, I, 537
- Tartara, London Method for**, IX, 100
- Tartrates**, I, 551  
 containing organic bases, tartaric acid in, I,  
 539  
 detection and estimation of, I, 537  
 See also under *Parent substance*.
- Tartrazin**, V, 133, 462, 578  
 detection of, V, 445
- Taurine**, VII, 246, 290
- Taurocholeic acid**, VII, 414
- Taurocholic acid**, VII, 413  
 estimation of, in bile, VII, 413, 417  
 preparation of, from bile, VII, 410
- Tea**, VI, 597; IX, 528  
 adulterations of, VI, 627, 629  
 analysis of, VI, 599, 602  
 after infusion, VI, 624  
 ash of, VI, 603  
 black, VI, 597  
 cape, VI, 602  
 caper, VI, 638  
 colouring matters in, V, 658; IX, 454, 529  
 detection of catechu in, VI, 620  
 of facings and colouring matters in, VI, 630  
 of foreign leaves in, VI, 631  
 of logwood in, VI, 630  
 of manganese in, VI, 632  
 of previously infused leaves in, VI, 627  
 estimation of caffeine in, 590, 606; IX, 526  
 by Dvorkowitsch's method, VI, 608  
 by Gomberg's process, VI, 612  
 by Stahlschmidt's method, VI, 606  
 of chlorophyll in, VI, 628  
 of essential oil in, VI, 628  
 of extract from, VI, 621  
 of fermentation products in, VI, 616
- Tea, estimation of gummy matters in**, VI, 629  
 of moisture in, IX, 528  
 of nitrogenous substances in, VI, 628  
 of resin in, VI, 629  
 of tannin in, V, 66, 88, 91; VI, 614; IX, 529  
 of theobromine in, VI, 612  
 of wax in, VI, 629  
 extract from, VI, 621  
 extraction of caffeine from, VI, 590, 606  
 flowers, dried, VI, 601  
 green, VI, 597  
 lie, VI, 639  
 microscopic examination of, VI, 633  
 oil, VI, 628  
 paraguay, VI, 641  
 preparation of, VI, 597  
 Read's test for, IX, 454  
 substitutes, VI, 638  
 tasting, VI, 626
- Tea-seed oil**, II, 69, 119; IX, 134
- Teel oil**. See *Sesame oil*.
- Temperature, comparison of Centigrade and  
 Fahrenheit degrees**, III, 619  
 maintainence of constant, I, 53
- Terebene**, IV, 426  
 painters', IV, 427
- Terebentene**, IV, 179
- Terpane**, IV, 170
- Terpene alcohols, cyclic**, IV, 254, 277  
 in essential oils, IV, 254  
 bromides, IV, 167  
 nitrosates, IV, 167
- Terpeneless essential oils**, IV, 429, 430
- Terpenes**, IV, 163, 165; IX, 324  
 constitution of, IV, 170  
 detection of in the presence of, sesquiterpenes,  
 IV, 174  
 dicyclic, IV, 179  
 constitution of, IV, 184  
 in essential oils, IV, 253  
 general characters of, IV, 168  
 monocyclic, IV, 170  
 nitrosochlorides of, IV, 167  
 and sesquiterpenes, distinction between, IV,  
 185
- Terpinene**, IV, 168, 171, 176; IX, 324  
 nitrosita, IV, 177
- Terpinenes, isomeric**, IX, 324
- Terpineol**, IV, 254, 280; IX, 343
- Terpineols, constitution of**, IV, 281
- Terpinolene**, IV, 168, 171, 176; IX, 324
- Terpinylacetate, detection of, in essential oils**, IX,  
 331
- Terra cotta**, R, V, 154
- Tetanine**, VII, 354
- Tetanotoxine**, VII, 354
- Tetrabromfluorescein**, V, 294
- Tetrabromo-dichlorofluorescein**, V, 296
- Tetracetyl aconine**, VI, 264
- Tetrachlorquinone**, III, 340
- Tetracoline**, VI, 155
- Tetraethylammonium chloride**, VI, 23  
 hydroxide, VI, 22  
 iodide, VI, 21  
 platinichloride, VI, 23

- Tetrahydroquinoline, VI, 155  
 Tetraiodofluorescein, V, 296  
     as an indicator, III, 556  
 Tetraiodo-phenolphthalein, III, 557  
 Tetraiodopyrrole, VI, 150  
 Tetralkylammonium bases, VI, 20  
     salts and amines, separation of, VI, 3  
 Tetramethyldiaminobenzophenone dyestuffs.  
     See under *Colouring matters*.  
 Tetramethylenediamine, VII, 347  
 Tetrathera oil, IV, 458  
 Tetrasalicylide, III, 499  
 Tetrazo-browns, V, 163  
 Tetrazo-colouring matters. See under *Colouring matters*.  
 Thalline, VI, 157  
     sulphate, VI, 158  
 Thann leaf extract, reactions of, V, 45  
 Thebaine, VI, 363, 365, 405; IX, 502  
     constitution of, VI, 356  
*iso*-Thebaine, IX, 502  
 Thebenine, VI, 406  
 Theine. See *Caffeine*.  
 Theobromine, VI, 591; VII, 322  
     in cacao beans, VI, 700  
     constitution of, VI, 580  
     estimation of, in cocoa, VI, 709  
     in tea, VI, 612  
     isomer of, IX, 525  
     in kola, VI, 682  
     salts of, VI, 593  
 Theocin, VI, 596  
 Theophylline, VI, 595; VII, 321  
 Thermifugin, VI, 159  
 Thermostat, Lowry, I, 52, 55  
 Thermostats, I, 53  
 Thiazines, V, 353  
     constitution of, V, 317  
 Thiazole yellow, V, 582  
     S, V, 374  
 Thiazoles, V, 370  
 Thioantipyrine, VI, 47  
 Thiocarmine, V, 462  
     R, V, 356, 467, 590  
     (Cassella), V, 358  
 Thiocatechin, V, 612  
 Thiocyanates, VII, 542  
     detection of, VII, 548  
     estimation of, VII, 550  
     insoluble, estimation of, VII, 555  
*iso*-Thiocyanates, VII, 547  
 Thiocyanic acid, VII, 542, 544  
 Thioflavine S, V, 373, 582  
     T, V, 461, 580, 582  
     TCN, V, 373  
 Thioform, III, 501  
 Thiogene black 6 BG conc., V, 564  
     blue JL, V, 596  
     brown GC, V, 618  
     catechu R, V, 620  
     dark blue, V, 600  
     red, V, 380  
     heliotrope, O, V, 610  
     new blue, BL, V, 598  
     olive green GGN, V, 572  
 Thiogene purple, V, 380  
     rubine O, V, 608  
 Thioindigo red B, V, 536  
     scarlet, V, 536  
 Thion blue black, V, 566  
     yellow (Kalle and Co.), V, 376  
 Thional black FC, V, 566  
     blue 2 B, V, 604  
     brilliant green GX, V, 576  
     green 2 G, V, 574  
     yellow R, V, 586  
 Thionine V, 454  
     blue V, 461  
     blue G, O extra, V, 356  
 Thiophen, III, 210  
     in benzene, III, 210  
     separation of, from commercial benzol, III, 235  
 Thiophene brown, V, 614  
 Thiophenol black BF extra, V, 568  
     T extra, V, 377  
 Thiophosphine J, V, 372  
 Thiopyrine VI, 47  
 Thiotoluene, III, 211  
 Thioxene, III, 211  
 Thioxine blacks, V, 378  
     brown G, V, 614  
     dark blue B, V, 604  
     indigo blue B, V, 604  
     orange, V, 376  
     R, V, 584  
     yellow G, V, 376, 584  
 Thorn tree bark, reactions of, V, 47  
 Thuja oil, IV, 458  
 Thujene, IV, 168, 184  
 Thujone, IV, 212  
 Thujyl alcohol, IV, 280; IX, 343  
 Thurston tester, III, 171, 182  
 Thyme oil, IV, 397, 458; IX, 376  
 Thymol, IV, 254, 288  
     colour-reaction of, with chloroform and alkali, III, 297  
     detection of, IV, 289  
     estimation of, in thyme oil, IV, 399  
     and menthol, separation of, IV, 290  
 Thyreoglobulin, VIII, 92  
 Tiglic acid, VII, 75  
 Tin, detection of, in organic substances, I, 75  
     in canned food, VIII, 337; IX, 612  
 Tinctures, estimation of alcohol in, I, 129; IV, 102  
     methylated spirit in, I, 95, 96  
 Tinfoil paper, I, 479  
 Tintometers, V, 439  
 Titan como SN, V, 592  
     TG, V, 602  
     ingrain blue, V, 592  
     scarlet V, 548  
 Titer test for fats and oils, II, 56  
 Tobacco, VI, 242  
     alkaloids in, IX, 477, 478  
     combustibility of, VI, 243, 244  
     effect of fertilizers on, VI, 244  
     estimation of nicotine in, VI, 240, 251; IX, 485  
     of non-volatile acids in, VI, 249  
     leaves, enzyme of, VIII, 15



- Tobacco, manufacture of, in England, vi, 249  
 poisoning by, vi, 241  
 smoke, vi, 251  
 hydrocyanic acid in, vii, 463
- Tocher's test for sesame oil, ii, 145
- Tolu balsam, iii, 459  
 adulteration of, iii, 460  
 analysis of, iii, 459; ix, 297  
 detection of colophony in, iii, 460  
 in Peruvian balsam, iii, 458  
 and Peruvian, and storax, distinctions between, iii, 454  
 syrup of, iii, 461
- Toluene, iii, 215  
 behaviour of, with benzal chloride, iii, 280  
 commercial, iii, 216  
 estimation of, in coal-tar distillates, ix, 230
- Tolhydroquinone iii, 337
- m*-Toluidine, vi, 64
- o*-Toluidine, v, 205; vi, 64, 109
- p*-Toluidine, v, 205; vi, 66  
 estimation of, in admixture with *o*-toluidine, vi, 69
- Toluidine blue, v, 461, 588  
 O, v, 356  
 commercial, vi, 67
- Toluidines, vi, 63  
 and benzylamine, physical distinctions between, vi, 64  
 distinctions between, *o*-, *m*- and *p*-, vi, 65  
*o*- and *p*-, separation and estimation of, vi, 67  
 specific gravity of mixtures of, vi, 70
- Toluresinotannol, iv, 4
- Tolusafranine, v, 338
- Toluylene bordeaux B, v, 556  
 dark blue GN, v, 602  
 red, v, 449
- Tolylene brown, v, 166, 612  
 G, v, 188  
 blue, v, 310  
 B for cotton, v, 338  
 orange, v, 578  
 G, v, 190  
 R, v, 188, 190, 578  
 red, v, 310, 321, 334, 461, 548  
 detection of, v, 445  
 yellow, v, 174
- Tolpyrine, vi, 46, 47  
 salicylate, ix, 492
- Tolysal, iii, 492
- Tomatoes, preserved, detection of salicylic acid in, iii, 479  
 tinned, separation of salicylic acid from, iii, 486
- Tormentil root, analysis of, v, 67
- Tormentil-tannin, v, 7
- Tóth's method for the estimation of nicotine and other alkaloids, vi, 240
- Trachylic acid, iv, 5
- Train oil, ii, 227  
 detection of, in rape oil, ii, 130
- Transformer oils, ix, 256
- Treacle, i, 355
- Trehalase in yeast, i, 212
- Triacetyl aconitine, vi, 262
- Triacetylene, ix, 228
- Triaminophenol, vi, 105
- Trianisoline, v, 306
- Triazol black B, v, 568  
 blue R, v, 600  
 bordeaux B, v, 556  
 brown G, OO, v, 618  
 fast yellow G, v, 584  
 pure blue R, v, 598  
 red 10 B, v, 554  
 violet B, N, v, 608  
 yellow G, v, 584
- Tribromocresol and tribromophenol, differences between derivatives of, iii, 300
- Tribromomethane. See *Bromoform*.
- Tribromophenol, iii, 299  
 and tribromocresol, differences between derivatives of, iii, 300
- Tribromophenoxides, iii, 299
- Tribromoresorcinol, iii, 337
- Trichloracetic acid, i, 272
- Trichloraldehyde. See *Chloral*.
- Trichorethylidene glycol. See *Chloral hydrate*.
- Trichlormethane. See *Chloroform*.
- Trichlorotri-iodo-linolenic acid, ix, 185
- Trichlorquinone, iii, 340
- Triethylamine, vi, 20
- Triglycerides, theory of saponification of, with alkali, ii, 12  
 table of the proportion of fatty acids and glycerol obtainable from, ii, 11, 12
- Trihydroxyanthraquinones, v, 211
- Triiodomethane. See *Iodoform*.
- Trillat test for methyl alcohol, i, 89
- Trimethylacetic acid, i, 524
- Trimethylamine, vi, 11, 14  
 and ammonia separation and estimation of, vi, 18; ix, 469  
 hydrochloride, vi, 17  
 physical properties of, vi, 12, 16  
 as a putrefaction product, vii, 352
- Trimethylcolchic acid, vii, 7, 8
- Trimethylhydroxyethylammonium hydroxide, See *Choline*.
- 2:4:6-Trimethylpyridine, vi, 145
- 1:3:7-Trimethylxanthine, vi, 581
- 2:6:8-Trioxypurine, vii, 357
- Trioxysparteine, vi, 234
- Triphenylamine, vi, 88, 97
- Triphenylbenzene. See *Benzerythrene*.
- Triphenylcarbinol and its salts, constitution of, v, 238
- Triphenylmethane, v, 231  
 behaviour of, with benzal chloride, iii, 280  
 colouring matters. See under *Colouring matters*.  
 reactions of, with metallic chlorides, iii, 277
- Triphenylpararosaniline, v, 234
- Triphenylrosaniline-disulphonic acid, v, 253
- Triphenylrosaniline-monosulphonic acid, v, 252
- Triphenylrosaniline-trisulphonic acid, v, 254
- Triple phosphate. See *Magnesium ammonium phosphate*.
- Tritopine, vi, 354, 364, 406
- Trona red, B 3, v, 552

- Tropæolin, D, v, 138**  
     G, v, 138  
     O, v, 137, 459  
     OO, v, 138, 145, 458, 580  
     OOO, v, 459  
     OOOO, v, 140  
     O or R, v, 135, 139  
     Y, v, 137, 139, 142  
     No. 1, v, 137, 139  
     No. 2, v, 139  
**Tropæolins, v, 137**  
**Tropeine, salicyl, vi, 301**  
**Tropeines, vi, 291**  
     artificial, vi, 301  
     detection of, vi, 303; ix, 491  
     estimation of, ix, 491  
     hydrolysis of, vi, 291  
     separation of, vi, 304  
**Tropic acid, vi, 292**  
**Tropine, vi, 293**  
     esters of, vi, 301  
     exhaustive methylation of, vi, 204  
**pseudo-Tropine, vi, 294**  
 **$\alpha$ -Truxilline, vi, 340**  
**Trypsin, viii, 9**  
     estimation of the proteoclastic power of, viii, 494  
**Tryptophane, vii, 250**  
     estimation of, viii, 87; ix, 563  
     separation of, from the hydrolysis products of protein, viii, 27  
**Tuberosc oil, iv, 458**  
**Tubocurarine, vi, 476**  
**Tung oil, ii, 70, 154; ix, 140, 144**  
     action of acids on, ii, 156  
     iodine on, ii, 156  
     on the skin, ii, 157  
     commercial, ii, 157  
     composition of, ii, 155  
     drying properties of, ii, 155, 156  
     elaidin test for, ii, 156  
     hexabromide test for, ix, 143  
     mixed fatty acids from, ii, 157  
     polymerisation of, ii, 155; ix, 141  
     refractive index of, ix, 192  
     use of, ii, 157  
     viscosity of, ii, 157  
**Turacin, viii, 559, 574**  
**Turkey-red, v, 226**  
     oil, ii, 167; ix, 145  
         action of water and ether on, ii, 168  
         analysis of, ii, 168  
         composition of, ii, 167  
         cottonseed, ii, 168  
         detection of adulterants in, ii, 171  
         iron in, ii, 171  
         olive, ii, 168  
         preparation of, ii, 167  
         specific gravity of, ii, 168  
**Turmeric, v, 408, 413, 580, 635, 636, 637**  
     dye, v, 456  
     oil, iv, 458  
**Turnbull's blue, vii, 506, 526**  
**Turner reaction for gurgun balsam, iv, 88**  
**Turpentine, American, iv, 75**  
**Turpentine, Bordeaux or French, iv, 76, 80**  
     common, iv, 75  
         detection of, in Venice turpentine, iv, 79  
     French, iv, 76, 80  
     Larch, iv, 76, 80  
     oil, iv, 249, 251, 400, 425; ix, 377  
         adulteration of, iv, 406, 414  
             with petroleum spirit, iv, 409  
         American, iv, 401; ix, 378  
         bromine thermal test for, iv, 244  
         commercial, iv, 403  
         constants of, iv, 407  
         detection of, in bay oil, iv, 315  
         essential oils, iv, 247  
         rosin spirit in, iv, 416, 421, 422  
         estimation of mineral oil in, iv, 417  
         petroleum naphtha in, iv, 414  
     Finland, iv, 402  
     French, iv, 401  
     fractional distillation of, iv, 411, 419  
     German, iv, 403, 426  
     Grecian, iv, 403  
     iodine absorption of, iv, 423  
     Indian, iv, 403  
     rotation of, iv, 405, 410  
     Russian, iv, 401; ix, 380  
     specific gravity of, iv, 408  
     substitutes of, iv, 415, 426  
         constants of, iv, 407  
     Swedish, iv, 402  
     vapour density of, iv, 408  
     varieties of, iv, 401  
     wood. See *Wood turpentine oil*.  
     Venice, iv, 76, 80  
         substitute, iv, 426  
**Turpentines, iv, 13, 74**  
**Turpethin, vii, 130**  
**Turwar bark, reactions of, v, 45; ix, 399**  
**Tussah silk. See under Silk.**  
**Tussol, vi, 46**  
**Twaddell's hydrometer, i, 7**  
**Typewriter ribbons, testing of, v, 687**  
**Typhoxine, vii, 354**  
**Tyrosinase, viii, 14**  
**Tyrosine, vii, 231**  
     and cystine, separation of, viii, 689; ix, 563  
     estimation of, viii, 87; ix, 563  
     separation of, from the hydrolysis products of proteins, viii, 27  
**Tyrotaxon, vii, 355**
- U**
- Ulmutannic acid, v, 7**  
**Ultramarine blue, v, 588**  
     detection of, as an impurity in sugar, i, 353  
**Umbellic acid, iii, 448**  
     occurrence of, in resins, iv, 3  
**Union black, 2 BNI, v, 568**  
**United States Army Ordnance 115° test for explosives, iii, 616**  
     method for the estimation of citric acid in fruit juices, i, 562  
     pharmacopœia method for the assay of opium, vi, 419  
     test for methyl alcohol, i, 88

- Urania blue, v, 356  
 Uranin. See *Chrysolin*.  
     G, v, 580  
 Urates, VII, 373  
     detection of, in urinary deposits, VII, 382.  
     See also under *Metals*.  
 Urea, VII, 288; VIII, 289  
     action of heat on, VII, 289  
     analogues of, VII, 286  
     detection of, VII, 293  
     estimation of, VII, 296; IX, 564  
     formation of, in the animal body, VII, 287  
     hydrochloride, VII, 293  
     nitrate, VII, 291  
     oxalate, VII, 292  
     preparation of, VII, 288  
     properties and reactions of, VII, 289, 293  
     salts of, VII, 291  
 Urethane. See *Ethyl carbamate*.  
 Uric acid, VII, 357; VIII, 289; IX, 570  
     calculi, VII, 387  
     detection of, VII, 366  
         in urinary deposits, VII, 382  
     effect of ingestion of atrophane on output of,  
         IX, 570  
     estimation of, VII, 368; IX, 571  
         in blood, IX, 572  
         by method of Folin and Denis, IX, 571  
     fermentation of, VII, 364  
     formula of, VII, 357, 364  
     iso-dynamic forms of, VII, 364  
     murexide test for, VII, 366  
     output of, IX, 570  
     preparation of, VII, 359  
     properties of, VII, 360  
     reactions of, VII, 360, 366  
     salts of, VII, 373  
 Urinary calculi, composition of, VII, 385  
     examination of, VII, 388, 390  
     deposits, VII, 380  
     examination of, VII, 381, 384  
 Urine, acids of, VII, 357  
     action of copper sulphate on, I, 396  
     analysis, I, 393  
     aromatic hydroxy acids in, VII, 404  
     benzoic acid in, IX, 574  
     colloidal nitrogen in, IX, 575  
     composition of, IX, 570  
     detection of aceto-acetic acid in, VII, 401  
         of acetone in, I, 107; VII, 401  
         of aniline in, VI, 58  
         of antipyrine in, VI, 43  
         of bile acids in, VII, 430  
             pigments in, VII, 425  
         of cinnamic acid in, IX, 291  
         of creatinine in, VII, 314  
         of cystin in, VII, 245  
         of dextrose in, I, 393, 395, 398  
         of hæmatoporphyrin in, VIII, 555  
         of homogentisic acid in, VII, 405  
         of  $\beta$ -hydroxybutyric acid in, VII, 400  
         of hydroxymandelic acid in, VII, 406  
         of *p*-hydroxyphenyl-acetic acid in, VII, 404  
         of *p*-hydroxyphenyl-propionic acid, VII, 404  
         of indirubin in, VII, 256  
     detection of indoxyl-sulphuric acid in, VII,  
         255  
         of kynurenic acid in, VII, 406  
         of Martins' yellow in, v, 126  
         of minute traces of sugar in, I, 398  
         of pentoses in, I, 400  
         of pyramidone in, VI, 49  
         of santonin in, VII, 156  
         of strychnine in, VI, 459  
         of thiocyanates, in VII, 543  
         of uric acid in, VII, 366  
         of uroleucic acid in, VII, 406  
     estimation of aceto-acetic acid in, IX, 577  
         of acetone in, I, 108; VII, 404; IX, 577  
         of amino-acids in by Henrique's method,  
             VII, 408  
         of creatine in, IX, 567  
         of creatinine in, VII, 315; IX, 567  
         of dextrose in, I, 394, 396, 397  
         of glucuronic acid in, VII, 399  
         of hippuric acid in, VII, 394; IX, 569  
         of  $\beta$ -hydroxybutyric acid in, VII, 403  
         of lactic acid in, IX, 583, 584  
         of pentoses in, I, 400  
         proteins in, by Devoto's method, VIII, 56  
             by Rebach's method, VIII, 58  
         of purine bases in, VII, 328  
         of urea in, VII, 296  
         of uric acid in, IX, 571  
     glucuronic acid in, I, 399  
     horses', preparation of potassium phenyl-  
         sulphate from, III, 400  
     isolation of creatinine from, VII, 311, 315;  
         IX, 565  
         of methyl-and dimethyl-guanidine from,  
             VII, 306  
         of purine bases from, VII, 326, 338  
     oxalic acid in, IX, 574  
     oxyproteic acids in, VII, 407  
     preparation of creatine from, IX, 565  
         of uric acid from, VII, 359  
     removal of proteins from, I, 393  
     sugars in, I, 393, 400  
     use of chloroform for preserving, I, 280  
 Uroferric acid, VII, 407  
 Uroleucic acid, VII, 406  
 Uropherin, III, 491  
 Ursol, D, P, DD, v, 314
- V
- Valenta test for butter fat, II, 299  
     for oils and fats, II, 62  
 Valentine's meat juice, VIII, 398, 402; IX, 614  
 Valeral, I, 255  
     presence of, in commercial amyl nitrite, I,  
         251, 252  
     valeric acid, I, 526  
 Valerates, commercial, I, 526  
 iso-Valerates, I, 524  
 Valerian oil, IV, 458  
 Valeric acid and butyric acid, distinction between,  
     I, 523  
     commercial, I, 526  
     from porpoise oil, II, 230

- iso*-Valeric acid, I, 524  
 and acetic acid, distinction between, I, 525  
 and caproic acid, distinction between, I, 525  
 separation and estimation of, I, 515, 525  
 of, from other organic acids, I, 525  
 Valeric acids, I, 524
- Valine, VII, 249  
 and *d*-alanine, separation of, IX, 562  
 the hydrolysis products of proteins, separation of, VIII, 25  
 leucine and *iso*-leucine, separation of, VIII, 25
- Valonia, V, 37  
 analysis of, V, 66, 67, 102  
 dyeing properties of, V, 55  
 reactions of, V, 42, 50
- Valonia-tannin, V, 7
- Vanilla, III, 514; IX, 306  
 analysis of, III, 517; IX, 306  
 essence of, III, 520  
 assay of, III, 522; IX, 308  
 detection of caramel in, III, 521  
 of coumarin in, III, 522; IX, 306  
 of resins in, III, 521  
 piperonal in, III, 518  
 Ritsert's tests for acetanilide in, III, 520
- Vanillic acid, III, 513
- Vanillin, III, 513; IX, 306  
 adulteration of, IX, 308  
 commercial, III, 515  
 and coumarin, separation of, III, 519; IX, 306  
 estimation of, III, 517; IX, 307  
 influence of, on tests for formaldehyde, I, 260  
 percentage of, in vanilla, III, 514; IX, 308  
 presence of, in beet sugar molasses, I, 356  
 reactions of, III, 516; IX, 307
- iso*-Vanillin, III, 522
- Vapour, densities of organic substances, determination of, I, 16
- Varnishes, lithographic, II, 356  
 resins used in, IV, 11
- Vaseline, III, 183  
 bromine absorption of varieties of, III, 183  
 oil, IX, 259  
 specific gravity of varieties of, III, 184  
 tests for the purity of, III, 185
- Vat dyes, V, 524  
 indigo, V, 570  
 blue, V, 588  
 red, V, 556  
 B.A.S., F.I B, V, 536
- Veal, composition of, VIII, 269
- Vegetable acids. See *Acids, vegetable*.  
 alkaloids. See *Alkaloids, vegetable*.  
 fats. See *Cacao-butter and Coconut-oil groups of fats*.  
 fibres, estimation of cellulose in, I, 435  
 Oleins. See *Olive-oil group of oils*.  
 products, analyses of, I, 451  
 substances, analysis of, I, 445, 450
- Vegetables, canned, colouring matters in, V, 650
- Velvrl, IV, 153
- Venice turpentine, IV, 76, 80
- Veratralbine, VII, 82, 87
- Veratric acid, III, 513
- Veratridine, VII, 71, 76
- Veratrine and atropine, distinction between, VI, 307  
 commercial, VII, 71
- Veratroidine. See *Veratralbine*.
- Veratrum album, alkaloids of, VII, 78  
 viride, alkaloids of, VII, 79
- Verbena oil, IV, 459
- Verdigris, I, 513
- Vermicelli, VIII, 102
- Vermilionette, V, 296
- Vermillion, use of, as a colouring matter for sweets, I, 358
- Vermin-killers, VI, 463
- Vert lumière, V, 278
- Vesipyrin, III, 505
- Vesuvine, V, 163, 458  
 detection of, V, 445
- Vetivene, IX, 347
- Vetivenol, IX, 347
- Vetivert oil, IV, 459; IX, 347
- Vicianin, VII, 103
- Vicilin, VIII, 111
- Victoria black B, V, 172  
 blue, V, 558  
 5 G, V, 558  
 blue, V, 445, 455, 588  
 B, V, 255, 284, 461, 590  
 BS, V, 255, 284  
 R, V, 255, 284  
 4 R, V, 255, 284, 461  
 green, V, 242, 453, 570  
 3 B, V, 284  
 navy blue LH, V, 596  
 pure blue B, V, 602  
 red, V, 192  
 violet, V, 606  
 4 B S, V, 156  
 yellow, V, 122, 462, 466, 576
- Vidal black, V, 560  
 for cotton, V, 377  
 S, for cotton, V, 377
- Vieille test for explosives, III, 612
- Vignin, VIII, 111
- Vigoral, IX, 614
- Vinasses, amines in, VI, 15
- Vinegar, I, 495; IX, 92  
 alcohol in, I, 498, 504  
 analyses of, I, 500  
 aromatic, I, 501  
 beer. See *Beer vinegar*.  
 cider. See *Cider vinegar*.  
 colouring matters, V, 655  
 commercial analysis of, I, 504  
 microscopic examination of, I, 504  
 composition of, I, 495  
 detection of arsenic in, I, 504  
 caramel in, IX, 96  
 cayenne pepper in, I, 504  
 copper in, I, 504  
 flies in, I, 504  
 ginger in, I, 504  
 lead in, I, 504  
 mineral acids in, I, 501, 503  
 oxalic acid in, I, 503  
 tartaric acid in, I, 496, 503

- Vinegar, detection of zinc in, I, 504  
 estimation of acetic acid in, I, 496  
 chlorine in, I, 502  
 free mineral acid in, I, 502; IX, 94  
 volatile acids in, IX, 92  
 glucose. See *Glucose vinegar*.  
 malt. See *Malt vinegar*.  
 mineral acids in, I, 501; IX, 94  
 solid extract from, I, 499  
 specific gravity of, I, 495  
 sugar. See *Sugar vinegars*.  
 wine. See *Wine vinegar*.
- Vinyl sulphide, IV, 300
- Vinyl-trimethylammonium hydroxide. See *Neurine*.
- Violamin B, v, 308, 546  
 3 B, G, 2 R, v, 308  
 R, v, 308, 468, 546
- Violamines, v, 301
- Violanthrene CD, v, 608
- Violet, acid. See under *Violet*.  
 alizarin. See under *Alizarin*.  
 alkali. See under *Alkali*.  
 amethyst, v, 328  
 aniline, v, 324  
 anthracene. See under *Anthracene*.  
 anthraquinone, v, 608  
 BN triazol, v, 608  
 BS gallanilic, v, 348, 462  
 3 B erio-chrome, v, 608  
 3 B extra, v, 280  
 4 BS, formyl, v, 606  
 5 B, 6 B, v, 272  
 benzyl, v, 258, 272, 461, 473, 604  
 black, v, 172, 558  
 C, v, 257  
 chrome. See under *Chrome*.  
 ciba. See under *Ciba*.  
 congo, v, 178, 606  
 crystal. See under *Crystal*.  
 diamine. See under *Diamine*.  
 direct. See under *Direct*.  
 Doebner's, v, 239  
 fast. See under *Fast*.  
 formyl. See under *Formyl*.  
 guinea. See under *Guinea*.  
 Hessian, v, 198, 604  
 Hofmann. See under *Hofmann*.  
 immedial. See under *Immedial*.  
 indanthrene. See under *Indanthrene*.  
 iodine, v, 278  
 iris, v, 328  
 methyl. See *Methyl violet*.  
 methylaniline, v, 256  
 naphthyl, v, 325, 334, 606  
 neutral, v, 320, 334, 461  
 oxamine, v, 186, 608  
 paraphenylene, v, 336, 461  
 Paris. See under *Paris*.  
 Perkins, v, 454, 604  
 phenyl, v, 604  
 R, 5 R and RR, v, 278  
 alizarin cyanol, v, 608  
 chloranisine, v, 608  
 columbia, v, 608
- Violet, R, oxochrome, v, 608  
 RRA, 3 RA, methylene, v, 334  
 5 R, rosanthrene, v, 610  
 regina, v, 606  
 rhoduline, v, 336  
 S wool, v, 154  
 solid, v, 348  
 S<sub>4</sub>B, ethylacid, v, 608  
 soluble regina, v, 284  
 spirit, v, 284, 604  
 victoria. See under *Victoria*.
- Violette's solution, use of, in the estimation of  
 reducing sugars, I, 333
- Viridic acid, VI, 646
- Viridine, VI, 129, 270
- Viridinine, VII, 353
- Vitellin, VIII, 92, 436  
 preparation of, VIII, 74
- Vitiatine, VII, 307
- Voisenet test for methyl alcohol, I, 90
- Vulcanite, IV, 143
- Vulcanized india-rubber. See under *India-rubber*.
- W
- Waagenboom, reactions of, v, 47
- Wagner's reagent for alkaloids, VI, 189
- Walnut oil, II, 70, 157; IX, 145  
 adulteration of, II, 158  
 black, II, 158  
 composition of, II, 157  
 constants of, II, 158; IX, 145  
 detection of linseed oil in, II, 353  
 of poppy oil in, II, 158  
 fatty acids from, II, 157  
 insoluble bromide test for, II, 29
- Waltham Abbey silvered vessel test for explosives,  
 III, 614
- Wanklyn and Fox's method for the estimation of  
 glycerol, II, 458
- Wanklyn's test for butter fat, II, 299
- Warrington's method for the analysis of wine lees,  
 I, 546
- Wartara oil, IV, 459
- Water blue, v, 252, 254, 284  
 B, BS, OO, v, 252  
 6 B, v, 252, 455  
 R, v, 455
- Water-gas pitch and coal-tar pitch, differences be-  
 tween, III, 33  
 tar, III, 34
- Water-soluble nigrosine, v, 327, 467  
 quinoline yellow, v, 360
- Wattle bark, v, 39  
 reactions of, v, 48
- Wax, Japan. See *Japan wax*.  
 white or bleached, II, 244
- Waxes, analysis of by saponification, II, 14  
 Buchner's numbers for, II, 256  
 classification of, II, 64  
 constants for, II, 250  
 constitution of, II, 7  
 determination of the acetyl value for, II, 32  
 hydrolysis of, II, 11

- Waxes**, identification of, II, 73, 87, 88  
     iodine value of, II, 29, 32  
     properties of, II, 1  
     proportion of glycerol and acid obtained from, II, 12  
     ratio of the acid and ester values of, II, 254  
     saponification of, II, 16  
     solid, II, 242  
     specific gravity of, II, 47, 250  
     unsaponifiable matter from, II, 261  
     yields of, from different seeds and nuts, II, 4  
**Wax-myrtle oil**, IV, 459  
**Weidel's test** for purine bases, VII, 331  
**Weingartner's tables** for the recognition of artificial colouring matters, V, 444  
**Weinwurm's test** for beeswax, II, 257  
**Weld**, V, 408, 411, 578, 634  
     extract, V, 637  
**Wetzel potash bulbs**, use of, I, 57  
**Whale oil**, II, 73, 227  
     constants for, II, 228  
     and drying oils, distinction between, II, 88  
     effect of blowing on, II, 367  
     extraction of, II, 228  
     fatty acids from, II, 229  
     group, II, 67, 73, 213  
     varieties of, II, 228  
     oils, hardened, IX, 123  
     insoluble bromide value for, II, 29  
**Wheat**, I, 453  
     edible pastes from, VIII, 102  
     farina, composition of, I, 464  
     flour. See *Flour*.  
     germ, composition of, I, 464  
     germs, isolation of betaine and choline from, VII, 279  
     mineral constituents, of, I, 456  
     oil, II, 70, 147  
         fatty acids from, II, 148  
     proteins of, VIII, 96  
     rolled, composition of, I, 464  
     shredded, composition of, I, 464  
     starch, I, 412, 415, 425  
**Whey**, VIII, 196  
**Whisky**, I, 201  
     American, I, 202  
     colouring matters in, V, 655  
     distillation of, I, 201  
**White bark**, reactions of, V, 48  
     fish oil, II, 226  
     spirit, IV, 426  
     tan. See under *Tan*.  
**Whiting liver oil**, II, 221  
**Wijs' method** for the estimation of the iodine value of fats and oils, II, 31  
**Will test** for explosives, III, 615  
**Williamson's blue**, VII, 506  
**Willow bark**, reactions of, V, 47  
     glucosides of, VII, 99  
**Wilson chromometer** for kerosene, III, 130  
**Wine lees**, Warrington's method for the analysis of, I, 546  
**Wine of quinine**, VI, 533  
     rectified spirit of, I, 111  
**Wines**, I, 165; IX, 13  
     acid in, I, 169, 170, 184; IX, 92  
     alcohol in, I, 183  
     analysis of, I, 165  
     ash from, I, 169, 184  
     Cazeneuve's test for, I, 178  
     detection of abrastol in, III, 402  
         of alkanet in, I, 181  
         of benzoic acid in, III, 410; IX, 280  
         of caramel in, I, 179  
         of cochineal in, V, 423  
         of colouring matter in, I, 177, 181, V, 642, 654  
         of dulcine in, VII, 303  
         of salicylic acid in, III, 477  
     estimation of ash from, I, 169  
         of boric acid in, I, 176  
         of cane sugar in, I, 171  
         of colouring matter in, V, 86  
         of extract from, I, 168  
         of fixed acid in, I, 170  
         of fluorides in, I, 176  
         of glycerol in, I, 166; IX, 221  
         of potassium sulphate in, I, 174  
         of reducing sugar in, I, 170  
         of saccharin in, I, 175  
         of salicylic acid in, I, 175; III, 483  
         of succinic acid in, IX, 97  
         of sulphurous acid in, I, 174  
         of tannin in, I, 175; V, 86, 88  
         of tartaric acid in, I, 177; IX, 13, 106, 109  
         of total acid in, I, 169  
         of volatile acids in, I, 169; IX, 92  
     extract from, I, 168, 183  
     glycerol in, I, 166, 183; IX, 221  
     physico-chemical analysis of, IX, 13  
     polarisation of, I, 171  
     potassium sulphate in, I, 174, 185  
     specific gravity of, I, 183  
     sugar in, I, 171, 185  
     sulphurous acid in, I, 170, 174, 186  
     tartaric acid in, I, 177, 539; IX, 13, 106, 109  
     wool test for, I, 178  
**Wine-vinegar**, I, 496; IX, 94  
**Wintergreen oil**, III, 493; IX, 305, 381  
     detection of free salicylic acid in, III, 496  
**Witt's tables** for the identification of colouring matters, V, 447  
**Woaded black**, V, 558  
**Wollny's butter refractometer**, II, 291  
**Wood**, dry distillation of, III, 12, 13, 19  
     estimation of cellulose in, I, 435  
     meal, III, 590  
     naphtha and its assay, I, 99  
     oil. See *Tung oil*.  
     pulp, I, 480  
         bleaching of, I, 483  
         fibres, microscopic appearance of, in paper, I, 475  
         manufacture of, IX, 81  
         moisture in, I, 481  
     spirit. See *Wood naphtha*.  
     turpentine oil, IV, 414, 424  
     vinegar. See *Pyroligneous acid*.  
**Wood-tar**, III, 19  
     creosote. See *Creosote, wood-tar*.

- Wool, VIII, 680  
 black, v, 164, 170, 558  
 blue S, v, 592  
 constituent dyes of compound shades on, v, 510  
 estimation of small quantities of, in cotton materials, IX, 623  
 examination of dyes on, v, 486, 489, 512  
 fast blue BL, v, 602  
 grey, v, 558  
   B, G, R, v, 338  
 green BS, v, 574  
   S, v, 284  
 mordanted vegetable colours on, v, 634  
 printing black B, v, 568  
 raw, analysis of, VIII, 682  
 reactions of, VIII, 684  
 red SB, v, 556  
 scarlet G, v, 548  
   R, v, 148, 548, 550  
   2 R, v, 550  
 and silk, distinction between, VIII, 646, 647  
 test for foreign colouring matter in wines, I, 178  
 violet, S, v, 154  
 Wool-fat, II, 495; VIII, 683  
 analysis of, II, 498, 502  
 composition of, II, 495  
 distillation of, II, 502  
 examination of, II, 497  
 saponification of, II, 495  
 saponification-equivalent of, II, 499  
 total acidity number of, II, 501  
 Wool-gelatin, VIII, 684  
 Wool-grease, detection of, in tallow, II, 212  
 distilled, II, 502  
 hydrocarbons distilled from, II, 503; IX, 228  
 Wool-keratin, VIII, 684  
 Wool-soap, VIII, 683  
 Wool-sweat, VIII, 683  
 Wool-wax, detection of, in beeswax, II, 261  
 unsaponifiable matter from, II, 261  
 Wormley's reagent for alkaloids, VI, 189, 307  
 Wormseed, estimation of santonin in, IX, 550  
 oil, IV, 427, 459; IX, 382  
   American, IV, 427, 459  
 Wormwood oil, IV, 428, 459  
   Japanese, IV, 428  
 Writing inks. See *Inks, writing*.  
 Wyeth's meat juice, VIII, 398; IX, 614

## X

- Xanthaline, VI, 354, 364, 406  
 Xanthates, I, 240  
 estimation of, I, 241  
 Xanthic acid, I, 240  
 Xanthin, v, 363  
 Xanthine, VI, 579; VII, 321, 327; VIII, 288  
 bases, detection of, IX, 525  
 estimation of, in meat extracts, VIII, 412  
 isolation of, VII, 326  
 calculus, VII, 387  
 colour reactions of, VII, 331  
 detection of, in urinary calculi, VII, 391

- Xanthine, Hoppe-Seyler's test for, VII, 331  
 salts of, VII, 330  
 Strecker's test for, VII, 331  
 synthesis of caffeine from, VI, 580  
 Weidel's test for, VII, 331  
 Xanthinoid compounds, behaviour of, with Kruger's reagent, VII, 325  
 Xanthocreatinine, VII, 317  
 Xanthone and its dyestuffs, v, 286  
 Xanthoresinotannol, IV, 4  
 Xylene, behaviour of, with benzal chloride, III, 280  
 blue BS, v, 600  
 commercial, III, 216  
 assay of, III, 219  
 Xylenes, III, 216  
 differences between *o*-, *p*- and *m*-, III, 218  
 estimation of *o*-, *m*- and *p*- in commercial xylene, III, 219  
 Xylidine ponceau, v, 451  
 red, v, 159, 548  
 scarlet, v, 148, 159  
 Xylidines, VI, 71  
 Xylol. See *Xylene, commercial*.  
 Xylonite, estimation of camphor in, IV, 199  
 use of camphor in the manufacture of, IV, 197  
 Xylose, I, 400  
 reducing power of, IX, 63

## Y

- Yara-yara, III, 259  
 Yeast, I, 205; IX, 15  
 action of, on maltose, I, 362  
 addition of starch to, I, 224  
 air, I, 219  
 and yeast foods, estimation of arsenic in, I, 148  
 ash of, I, 208  
 carbohydrates of, I, 209  
 catalase in, I, 213  
 cell contents, I, 207  
 cellulose, I, 209  
 cell-wall of, I, 206  
 characterisation of *Saccharomycetes*, I, 210  
 chemical composition of, I, 207; IX, 15  
 testing of, I, 221; IX, 15  
 circulation of, in nature, I, 214  
 classification of, IX, 15  
 coagulating enzymes (rennet) in, I, 212  
 culture, I, 214  
 determination of acidity of, I, 224  
   of the fermenting power of, by Hayduck's method, I, 223; IX, 16  
   by Kusserow's method, I, 223  
   by Meissl's method, I, 222, 223  
 diastase in, I, 212  
 distillery, II, I, 215  
 dry, I, 220; IX, 16  
 effect of heat on, I, 210  
   of light on, I, 210  
 enzymes in, I, 211; IX, 15  
 extracts, detection of, in meat products, VIII, 416  
   the activity of, VIII, 8  
   in, IX, 616



- Yeast, fat content of, I, 208  
 glycogen, I, 209  
 glycogen-spitting enzyme in, I, 212  
 in baking, I, 219  
 invertase in, I, 211  
 lactase in, I, 212  
 maltase in, I, 211  
 melibiase in, I, 211  
 microscopical examination of, I, 205, 220  
 nitrogenous constituents of, I, 208  
 oxidising enzyme in, I, 212  
 pectose, I, 209  
 physical examination of, I, 205, 220; IX, 15  
 proteolytic enzyme (endotryptase) in, I, 212  
 publications on, I, 225  
 pure culture of, I, 216, 218  
 raffinase in, I, 212  
 reducing enzymes in, I, 213  
 spore formation, I, 210  
 tannin in, I, 209  
 trehalase in, I, 212  
 variation of *saccharomycetes*, I, 214  
 vitality of, I, 210  
 zymase in, I, 213
- Yellow, acid. See under *Yellow*.  
 acme, V, 139  
 acridine, V, 366, 461  
 alizarin. See under *Alizarin*.  
 alkali. See under *Alkali*.  
 aniline. See under *Aniline*.  
 anthracene. See under *Anthracene*.  
 arnica, V, 158  
 azo acid, V, 139  
 B, chlorazol fast, V, 586  
 berries, V, 408  
 brazil wood, V, 408  
 brilliant. See under *Brilliant*.  
 carbazol, V, 180, 580  
 chloramine, V, 372  
 chrome. See under *Chrome*.  
 chrysoidine, V, 576  
 clayton, V, 143, 374, 580  
 congo, V, 178  
 coralline. See under *Coralline*.  
 cotton. See under *Cotton*.  
 crumpsall. See under *Crumpsall*.  
 D, salicene, V, 586  
 diamond. See under *Diamond*.  
 diamine. See under *Diamine*.  
 diphenylamine, V, 141, 145  
 direct. See under *Direct*.  
 eclipse. See under *Eclipse*.  
 fast. See under *Fast*.  
 fat colour, V, 156  
 G, cresotin, V, 582  
 domingo chrome, V, 586  
 Philadelphia, V, 363  
 R, Prager, alizarin, V, 154  
 thioxine, V, 376, 584  
 GG, chloranisine, V, 586  
 pyrazine, V, 586  
 GH, cloth, V, 584  
 GR, eriochrome, V, 584  
 indanthrene, V, 535  
 G, helindone, V, 535
- Yellow, 3 GR, algole, V, 535  
 4 G, stilbene, V, 586  
 5 G, sulphon, V, 586  
 gold, V, 125, 139  
 Heligoland, V, 174  
 Hessian, V, 198, 578  
 immedial. See under *Immedial*.  
 imperial. See *Aurantia*.  
 Indian, V, 139, 146; VII, 395  
 (Kalle and Co.) thion, V, 374  
 Manchester, V, 125, 145  
 Martius, V, 125, 457, 462  
 mekong. See *Mekong yellow*.  
 metanil. See *Metanil yellow*.  
 Mikado. See under *Mikado*.  
 milling. See under *Milling*.  
 M, pyrogene, V, 376  
 N, V, 146, 580  
 (Poirrier), V, 458  
 naphthol. See under *Naphthol*.  
 naphthylamine, V, 125  
 new. See under *New*.  
 nitrazine, V, 582  
 OO, V, 138  
 oriol, V, 140, 143  
 Persian, V, 140, 143  
 primuline, V, 578  
 quinoline. See under *Quinoline*.  
 R, cibanone, V, 535  
 krogene, V, 586  
 thional, V, 586  
 2 R, dianil, V, 584  
 resorcin, V, 139, 142  
 S, solid, V, 144  
 sulphanil, V, 178  
 sulphonated azo-dyes, V, 137, 141  
 sun, V, 132  
 T, V, 139  
 thiazole. See under *Thiazole*.  
 tolylene, V, 174  
 triazol. See under *Triazol*.  
 victoria, V, 122, 462, 466, 576  
 W, V, 138
- Yellow-fast-to-soap, V, 140, 143  
 Ylang-Ylang camphor, IV, 287  
 oil, IV, 459; IX, 382, 383  
 Yoghout, VIII, 227  
 Yohimbenine, VII, 94  
 Yohimbine, VII, 94  
 Yohimboa bark, alkaloids of, VII, 93  
 Yohimboic acid, VII, 94  
 Yopon, leaves of, VI, 642  
 Yorkshire College method of tannin assay, V, 63
- Z
- Zanzibar copal, IV, 51  
 Zedoary oil, IV, 459  
 Zein, VIII, 106  
 Zeisel and Panto's method for the estimation of  
 glycerol, II, 461, 466, 477  
 method for the determination of methoxyl  
 numbers of essential oils, IV, 240

Zeiss' butyro-refractometer, II, 291

Zinc cyanide, VII, 476

  detection of, in organic substances, I, 75

  in vinegar, I, 504

  estimation of, in cyanide solutions, VII, 495

  lactate, VII, 447

Zinc oleate, II, 412

  phenol-*p*-sulphonate, III, 395

  sarcolactate, VII, 450

Zingiberene, IV, 186; IX, 325

Zymase, VIII, 8

Zymase in yeast, I, 213







